

Alternation of Melting Points in Homologous Series of Long-Chain Compounds

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Abstract

The different possibilities of stacking of layers in long-chain compounds have been analyzed with reference to structural differences between even and odd members of homologous series. It has been possible to correlate packing differences with alternation of melting points and explain the alternation behavior completely on this basis. The theory can also be applied to surface films and mesomorphic phases. Alternation of enantiotropic transition temperatures and other physical properties are also discussed.

Introduction

THE OCCURRENCE OF ALTERNATION in melting points between even and odd members in homologous series of long-chain compounds has been known for a long time. According to the earlier theories this phenomenon was thought to be caused by alternation along the hydrocarbon chain of weak and strong bonds or of positive and negative charges on the carbon atoms (1). Later Müller (2) explained the alternating properties on the basis of the fact that the terminal groups are *trans* with respect to one another in even series, whereas they are *cis* in odd ones. Malkin (3) noticed, however, that the melting points never alternate when the chains are vertical in relation to the end group planes. From geometrical considerations he then put forward a hypothesis according to which the hydrocarbon chains in non-alternating series are vertical whereas they are tilted in alternating ones. Malkin's rule has later been criticized (4,5) as the β' -form of simple glycerides was found to give nonalternating melting points although the chains are tilted. According to a theory by Gorin et al. (6) the alternation properties are due to stronger bonds in even members caused by a kind of resonance, i.e., their ideas are somewhat similar to those of Beach (1). The only crystal forms of fatty acids which can be in equilibrium with the melt are the forms *C* and *C'* of even and odd members, respectively, and the melting point curve of the odd members is lower than that of even ones. Von Sydow (7) estimated the van der Waals interaction over the methyl gap in the two forms and found better interaction in even members in accordance with their comparatively higher melting points.

Quite recently Breusch (8) has reported studies of homologous series of long-chain compounds with respect to the occurrence of alternating physical properties. No explanation of the alternation behavior is, however, discussed.

In connection with an investigation of the solid state behavior of glycerides (9) the present author suggested that the alternating properties can be fully explained on the basis of the appearance of the terminal end group planes. A detailed analysis of the end group planes in this respect will be given here, and it appears that this simple consideration explains the alternating behavior of all series where the end group structure is known.

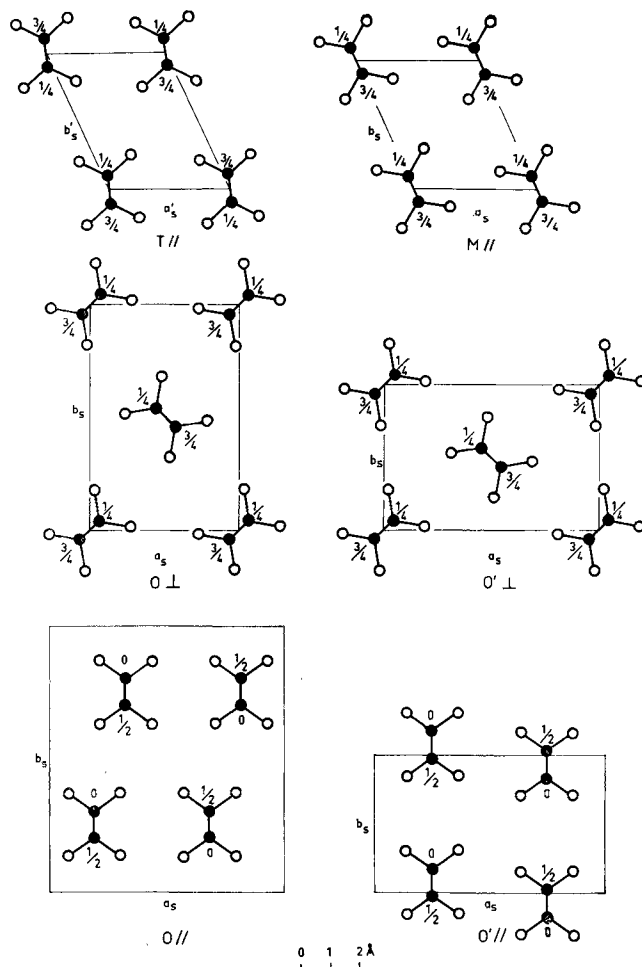


FIG. 1. Subcells corresponding to different close-packing of hydrocarbon chains.

The most common type of molecular packing will be regarded here where the molecules form layers, and the layers are stacked so that terminal planes of methyl groups are in contact. Long chain structures with other terminating groups than methyl groups in the layer boundary can be treated analogously.

Methyl End Group Planes

The packing of the hydrocarbon chains in long-chain compounds can be described by a subcell corresponding to the smallest repetition unit within the chain layer. The subcells of the different packing modes of parallel chains found up to now will be briefly described as their geometry is required for the further discussion. They are illustrated in Figure 1 and their dimensions will also be specified as different choice of subcell units occur in the literature.

The structure of the triclinic chain packing *T*// was determined by Vand and Bell (10). If a small error in their calculation of dimensions is corrected the following dimensions are obtained (11):

$$a_s = 4.41 \text{ \AA}, b_s = 5.40 \text{ \AA}, c_s = 2.45 \text{ \AA}, \\ a_s = 74.8^\circ, \beta_s = 108.5^\circ, \gamma_s = 120.5^\circ$$

The subcell section perpendicular to the chain axis is shown in Figure 1 (a'_s and b'_s are orthogonal axes corresponding to a_s and b_s respectively).

The monoclinic chain packing $M\parallel$ was first found by Abrahamsson and Westerdaahl (12) in 3-thiadioecanoic acid, where the subcell was somewhat distorted. The same packing occurs also in racemic 1-monoglycerides (13) and the subcell dimensions there are:

$$a_s = 4.26 \text{ \AA}, b_s = 4.83 \text{ \AA}, c_s = 2.57 \text{ \AA}, \gamma_s = 114.5^\circ$$

The common orthorhombic chain packing $O\perp$ was early analyzed by Bunn (14). Its subcell dimensions are very sensitive to thermal oscillation and the following values appear to be representative for temperatures well below the melting point of corresponding crystal forms:

$$a_s = 4.90 \text{ \AA}, b_s = 7.41 \text{ \AA}, c_s = 2.54 \text{ \AA}$$

A new orthorhombic chain packing $O'\perp$ closely related to the common one ($O\perp$) has been described by Abrahamsson (15). The subcell dimensions are:

$$a_s = 7.43 \text{ \AA}, b_s = 5.01 \text{ \AA}, c_s = 2.50 \text{ \AA}$$

In these two chain packing modes (and only there) the planes of every second carbon chain are perpendicular to the planes of the others.

There are also two orthorhombic chain packings with all chain planes parallel where the primitive subcell contains two chains. One packing called $O\parallel$ found by von Sydow (16) has following dimensions:

$$a_s = 8.15 \text{ \AA}, b_s = 9.21 \text{ \AA}, c_s = 2.55 \text{ \AA}$$

The other $O'\parallel$ resembles $O\parallel$ considerably. Abrahamsson and Ryderstedt-Nahringbauer (17) have described this packing with the following subcell:

$$a_s = 7.93 \text{ \AA}, b_s = 4.74 \text{ \AA}, c_s = 2.53 \text{ \AA}$$

Stanley (18) has recently reported the crystal structure of strontium caprylate hydrate and the same chain packing is evidently present there.

The detailed arrangement of the hydrocarbon chains in the hexagonal chain packing, H , is still unknown. It was discussed by the present author in connection with its occurrence in glycerides (9), and evidence was given indicating that there is large torsional oscillation of the chains. Whatever movement actually occurs, the experimental data indicate that the overall distribution of atoms around the chain axis has cylindrical symmetry. The dimensions of the hexagonal chain packing vary considerably with temperature (9), but are roughly $a_s = 4.9 \text{ \AA}$ and $c_s = 2.5 \text{ \AA}$.

Vand (19) suggested that the arrangement in layers can be classified by giving the subcell indices of the layer boundary. This system will be used here to define the methyl end group planes. Thus will, e.g., the C -form of fatty acids be described as $O\perp(0,2,1)$ giving a well-defined picture of the methyl end group planes.

Alternation or Nonalternation of Melting Points

The subcell regularity of the layers is unchanged at displacements along the chain axes an integral number of c_s -units. Different angles of tilt of the chains towards the end group planes are therefore possible for every chain packing. In the following discussion we will consider layers where only methyl

groups constitute the terminal planes, as, e.g., the layers of double molecular length in dimeric structures of normal fatty acids. The molecular arrangement within the layers in homologically isomorphous series is the same in even and odd members but the stacking of the layers can be different. It is suggested here that the alternation of melting points depends only on differences in packing densities at the layer interface.

If the hydrocarbon chains are vertical in the layers the van der Waals interaction over the methyl gap is the same in even and odd members, and in accordance with this the melting points do not alternate. Also when the chains are tilted the methyl end group planes can have the same structure in even and odd members. Alternation of the melting points is to be expected when the structure of the terminal planes is different in even and odd members which is the usual situation when the chains are tilted.

The conditions for nonalternation in series with tilted chains, according to the mechanism suggested above, will now be considered in terms of end group structure. If the carbon chain planes are all parallel, the end group planes possess the same structure in even and odd if (and only if) the projection of the chain axes on the end group planes are perpendicular to the intersections of the chain zig-zag planes with the end group planes, i.e., when the chains are tilted in a direction perpendicular to the planes through the carbon zig-zag chains. Also in the two chain packings where every second chain plane is perpendicular to the others it is possible to have very similar end group structures for even and odd. The structure of the terminal planes for different chain packings which should give nonalternation of the melting points will be specified below.

There are no possible end group planes for layers with triclinic chain packing $T\parallel$ with the same appearance of the methyl group region in even and odd members. For the monoclinic chain packing $M\parallel$, however, the end group planes $M\parallel(n,0,1)$ always have the same structure. In simple structures where the terminal groups lie strictly in planes, n is always an integer, whereas in compounds such as glycerides, where the chains of the molecule do not possess translational freedom in relation to each other, the end group planes can have indices $M\parallel(\frac{1}{2},0,1)$, $M\parallel(\frac{1}{3},0,1)$ and so on. Such cases (corresponding to the occurrence of terraces of end groups) need not be analyzed separately, the only differences being that n in the index condition does not necessarily have to be an integer. The conditions for equal end group structure in even and odd members when the chain packing is $O\parallel$ or $O'\parallel$ are $O\parallel(n,0,1)$ and $O'\parallel(n,0,1)$ respectively.

Belitskus and Jeffrey (20) have recently determined the crystal structure of peroxypelargonic acid, and the end group planes are evidently $O'\parallel(2,0,1)$ which is in accordance with the index condition given above for nonalternation for this chain packing. The corresponding series of aliphatic peroxy acids studied by Parker et al. (21) form homologically isomorphous crystal structures and the melting points are non-alternating in agreement with our theoretical consideration.

The end group planes in the low-melting form of oleic acid are also $O'\parallel(2,0,1)$ (17). If there are crystal forms in the series $\text{CH}_3(\text{CH}_2)_m\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$, which are homologically isomorphous with this structure, the situation is the same as in the

peroxyacids so that the melting points should not alternate. As the chains are bent at the *cis*-double bond (17) odd members of the series $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_m\text{COOH}$, however, cannot be homologously isomorphous with the low-melting form of oleic acid. Members C_{22} to C_{25} of this series, kindly supplied by S. Stenhagen, were therefore studied and as expected showed alternation of melting points. No polymorphism was observed and x-ray powder diffraction data indicate that odd members are isostructural with the high-melting form of oleic acid.

When the chains are arranged according to the orthorhombic subcells $O\perp$ and $O'\perp$ there are no end group planes with exactly the same structure in even and odd members. There is, however, very close resemblance between even and odd when the terminal planes are $O\perp(0,n,1)$ or $O\perp(n,n,1)$ and $O'\perp(n,0,1)$ or $O'\perp(n,n,1)$ respectively with n equal to odd values only, or when the plane indices are $O\perp(n,0,1)$ and $O'\perp(0,n,1)$ with n equal to $\frac{1}{2}$, $\frac{3}{2}$ and so on. The end group plane in the β' -form of triglycerides is $O\perp(1,1,1)$ and this series does not alternate. The methyl end group region there, which is the same as in the B' -form of *n*-pentadecanoic acid (22) is illustrated in Figure 2. It seems plausible that the packing density over the methyl gap will be roughly the same in even and odd; thus, we should expect nonalternation.

Any end group plane in layers of chains packed according to the hexagonal subcell has the same appearance for even and odd members, as the terminal groups have rotational symmetry. The α -form of racemic 1-monoglycerides are tilted, and the melting points do not alternate (9) in accordance with our theory. On cooling, this α -form is reversibly transformed into a β' -form (sub- α according to earlier nomenclature, cf. Ref. 9) and the transition temperature alternates. The end group planes of the β' form are $O\perp(0,2,1)$, i.e., even and odd members differ in end group structure there contrary to the situation in the α -form. The transition point corresponds to the intersection between the free energy curves of the two forms, and as the free energy alternates for the β' -form (due to differing end group structures) but not for the α -form the intersection points will also alternate.

The discussion on alternation of melting points can thus be generalized to be valid also for enantiotropic transition temperatures, even if the situation is more complex there, involving end group structures of both crystal forms. If the end group planes are equivalent for even and odd members of the two forms (according to the conditions given above) the transition temperatures should not alternate, whereas even if only one form possesses end group planes

differing in structure between even and odd the transition temperatures should alternate. When the end group planes are different in both forms, nothing definitely can be said about the alternation properties but as a rule they should alternate.

It is quite obvious that conditions for equal end group structure when the chains are packed with their axes crossed can be specified analogously. Such arrangements are reported for potassium soaps (23), amides (24) and for 11-aminoundecanoic acid hydrobromide (25). According to the known crystal structures it is evident that the methyl end group planes are different in even and odd members of these compounds, which corresponds to nonalternating melting points.

One should also expect alternation in other physical properties referring to the solid state than melting points when there are packing differences in the methyl group region between even and odd members. As mentioned earlier Breusch (8) has investigated homologous series with alternating melting points with respect to alternation in other properties. For constants corresponding to the solid state he reported alternation in solubilities but not in density. It should be noticed, however, that the limits of error of the density determinations (claimed to be $\pm 0.5\%$) are probably higher than the density deviations which are to be expected from differences in end group structure in homologously isomorphous long chain series.

In this connection it is very interesting to compare the behavior of certain monomolecular surface films investigated by Mrs. Lundquist at this Institute. One tilted phase of ethyl esters of *n*-fatty acids was found to show alternation of melting points (26). This indicates the existence of order of the chains in the film, i.e., the occurrence of a chain packing of the same type as in the crystalline state. If the chains were arbitrarily disordered the end group planes would be similar in even and odd members (cf. the α -form of 1-monoglycerides discussed earlier). If the planes of the carbon chains are ordered in some way, however, the end group planes can be different in even and odd members which may correspond to such differences in packing density of the methyl group region that the melting points should alternate.

There are some long-chain compounds exhibiting thermotropic mesomorphism, i.e., there is a transition below the melting point into a liquid crystalline state with some kind of translational freedom of the molecules. The fundamental work on mesomorphous phases by Luzzati and his school (27) has shown that the structure of the hydrocarbon chains is the same as in liquid *n*-paraffins. According to our theory it is obvious then that the melting points should not alternate.

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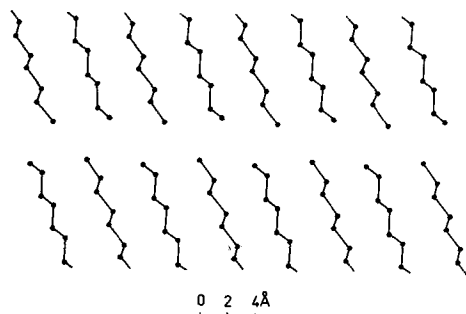


Fig. 2. Methyl end group region in the β' -form of *n*-pentadecanoic acid illustrating end group planes $O\perp(1,1,1)$.

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