

# Infrared Anisotropy and Structure of Crystalline Methyl Stearate and Methyl Octadecyl Sulfonate

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## Abstract

Infrared spectra of highly oriented crystalline films of methyl stearate and methyl 1-octadecyl sulfonate have been obtained using polarized radiation with the electric vector parallel and at 45° to crystallographic axes. The anisotropy of methyl stearate is in good agreement with the known structure and with vibrational assignments. The results obtained on the methyl ester of octadecyl sulfonic acid suggest a crystallographic plane (or glide plane) of symmetry. The hydrocarbon chains are tilted with respect to the end-group planes. The zigzag planes are roughly parallel to each other and perpendicular to the *ac* plane. Qualitative conclusions are drawn regarding the packing of the polar end-groups. Vibrational assignments are proposed for most prominent absorption bands.

## Introduction

A NUMBER OF CRYSTALLINE aliphatic carboxylic acids have in recent years been investigated by methods of polarized infrared spectroscopy (1-5). These studies have led to new information on polymorphism (2,5), to a better understanding of the spectra of aliphatic chain-molecules (1-4) and to new structural information (1,2,5). Two techniques have been used: investigation of single crystals of proper dimensions (2,5) and investigations on oriented films between infrared transparent plates (1,3,4). The former approach has been applied to all previously known modifications of octadecanoic and hexadecanoic acids; a new modification was discovered and characterized (2,5). The second approach has been applied to form C stearic acid and to vaccenic acid (1), all crystalline modifications of odd-numbered long-chain acids (3) and to adipic acid (4). In the case of form C stearic acid, which has been studied by both techniques, the results obtained on single crystals (2) and on thin films (1) were in good agreement.

The present investigation extends these studies to methyl esters of long-chain acids. Methyl stearate and methyl 1-octadecyl sulfonate have been investigated as thin films. The results on methyl stearate are in good agreement with its known structure. They might

serve as a starting point for the study of more complex structures, such as glycerides. The structure of long-chain methyl sulfonates does not appear to have been studied. The amount of available infrared data is also limited. In this communication an interpretation is suggested for major absorption bands between 400 and 3600 cm<sup>-1</sup> and a schematic structure is proposed for the crystalline modification obtained from the melt.

## Experimental

Thin crystalline films were prepared by slow cooling of molten samples between sodium chloride plates under the influence of a temperature gradient (1,6). Cesium bromide plates were used for the 400-700 cm<sup>-1</sup> region of methyl 1-octadecyl sulfonate. The orientation of crystalline methyl stearate with respect to the supporting plates was established by a polarizing microscope and by internal comparison of spectra obtained with the electric vector of the linearly polarized beam in various orientations with respect to the sample, as previously described (1,3,4). The (001) faces (the planes of end-groups) were parallel to the supporting plates, as in stearic acid samples prepared in the same manner (1). The crystal form was verified by powder diffraction measurements. Spectra were recorded with the electric vector (i) along the *a* axis and the *b* axis (perpendicular incidence); (ii) at ±45° to *a* while perpendicular to *b*; (iii) at ±45° to *b* while perpendicular to *a*. The data were internally consistent and in agreement with the monoclinic symmetry. Analogous measurements were carried out on methyl 1-octadecyl sulfonate. Very highly oriented samples leading to a consistent set of polarized spectra were obtained. The conclusions regarding orientation and structure are discussed further below.

The spectra were recorded on a Perkin-Elmer Model 21 instrument with sodium chloride optics and a six-plate silver chloride polarizer, and a Beckman IR-7 prism-grating instrument equipped with a beam condenser and polarizer. Because of certain design features, and the polarizing properties of the grating, the bulk of polarization data were obtained on the prism instrument. The efficiency of the polarizer and uniformity of sample orientation can be judged by Figures 1 and 2 which show several bands with

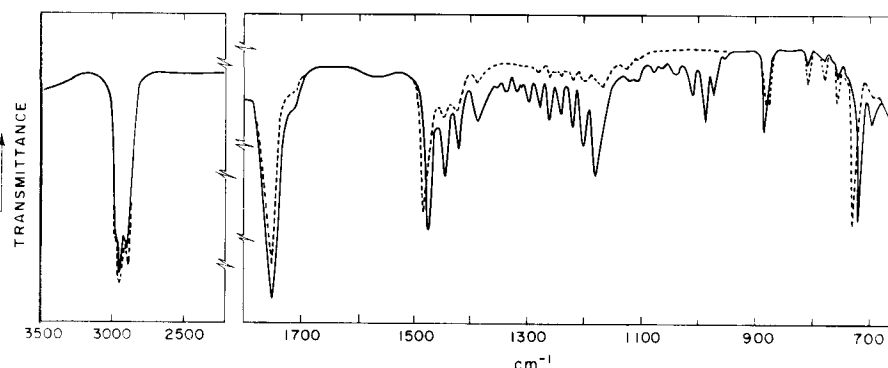


Fig. 1. Infrared spectrum of methyl stearate. Electric vector along *a* (solid line) and *b* (dotted line).

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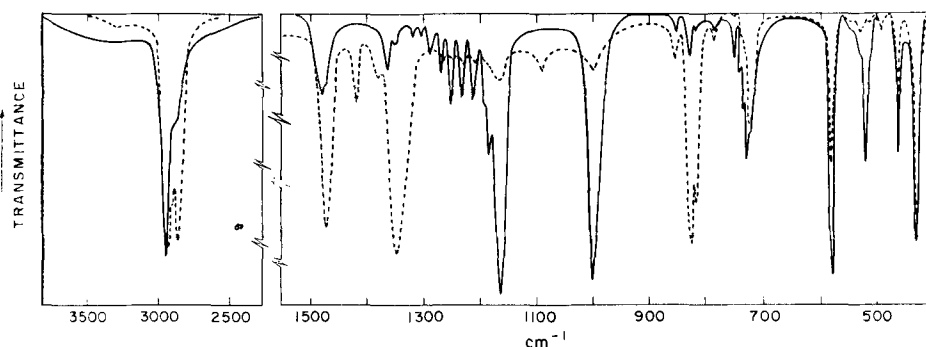


Fig. 2. Infrared spectrum of methyl 1-octadecyl sulfonate. Electric vector along *a* (solid line) and *b* (dotted line).

measurable components only along a single crystallographic axis. Commercial methyl stearate of highest available purity was used after recrystallization and analysis by gas chromatography. The sample of methyl 1-octadecyl sulfonate was supplied by J. S. Showell of this Laboratory. Its preparation and properties have been described (7).

## Results and Discussion

### Methyl Stearate

In monoclinic crystals molecular modes are split into components polarized along the *b* axis and within the *ac* plane, respectively. Polarization within the *ac* plane is in general difficult to evaluate and to interpret, because frequency-dependent dielectric properties must be taken into consideration (4b). For molecules containing long  $(\text{CH}_2)_n$  chains, the picture is simplified because the polarization of  $\text{CH}_2$  group-vibrations is essentially determined by the pseudo-symmetry describing the repetition in and of the hydrocarbon chains (1-4,8,9).

TABLE I  
Polarized Infrared Spectrum of Methyl Stearate

cm <sup>-1</sup>	Int.	Pol. <sup>a</sup>	Assignment <sup>b</sup>
3020	vw	b,ac	OCH <sub>3</sub> a.s.
2990	w	b > ac	OCH <sub>3</sub> s.s.
2955	m	b > ac	CH <sub>3</sub> a.s.
2925	vs	b	CH <sub>2</sub> a.s.
2920	vs	ac ⊥	}
2853	vs	ac ⊥	
2850	vs	b	CH <sub>2</sub> s.s.
1742	vs	b,ac ⊥	C=O s.
1474	s	b	}
1464	s	ac ⊥	
1436	m	ac ∥	CH <sub>2</sub> b.
1413	m	ac	OCH <sub>3</sub> b.
1380	m	b,ac	α CH <sub>2</sub> b.
1332	m	}	CH <sub>3</sub> b.
1312	m		
1293	m		
1274	m		
1265	m		
1235	m		
1215	m		
1197 <sup>c</sup>	m		
1177 <sup>c</sup>	s		
1164	w		
1121	w		
1105	w		
1044	w	ac	}
1036	w	ac	
1010	m	ac ∥	
987 <sup>c</sup>	s	ac ∥	
971	m	ac ∥	
954	w	b	
883	s	b,ac ⊥	
879	m	b	
843	w	b	
810	w	b,ac ⊥	
782	w	b,ac	(CH <sub>2</sub> r.)
761	w	b,ac ⊥	(CH <sub>2</sub> r.)
746	w	b	(CH <sub>2</sub> r.)
732	s	b	}
721	s	ac ⊥	
721	s	ac	
700	m	ac	

<sup>a</sup> Abbreviations: ac, polarized within the *ac* plane; b, polarized along the *b* axis; ⊥, perpendicular to molecular axes; ∥, parallel to molecular axes.

<sup>b</sup> Abbreviations: s.s.—symmetric stretching; a.s.—antisymmetric stretching; b.—bending; r.—rocking; w.—wagging.

<sup>c</sup> Bands essentially associated with C—O stretching motions.

The crystal structure of the stable form of methyl stearate is known from x-ray diffraction studies (8). It resembles somewhat the structure of form B stearic acid (9). The structure is monoclinic, space group  $C_{2h}^2-A2/a$ , eight molecules per unit cell. The molecules form sheets, with the molecular chains tilted  $63^\circ$  with respect to the *ab* planes (the planes of endgroups). The hydrocarbon chains are packed into an orthorhombic substructure (8,9) closely resembling crystalline polyethylene (10). The chemical bonds within the ester groups, if pictured as interatomic connecting lines, have strong components in the *ac* plane, weaker ones along the *b* axis. The structure is pictured in reference (8). The infrared spectra of such chain molecules can, in a first approximation, be interpreted by focusing attention separately on modes arising from the regular hydrocarbon packing and on modes localized essentially in the endgroups (1,2).  $\text{CH}_2$  modes of rotatory origin (wagging, rocking) give rise to "progressions," depending on chain length, while for modes associated with internal  $\text{CH}_2$  vibrations (stretching, bending), as observed under moderate resolution, no series of frequencies are observed (1,2,11).

The spectra obtained with the electric vector of the radiation beam parallel to the *a* and *b* axes are shown in Figure 1. Table I lists the frequencies, assignments and polarization characteristics of the observed bands. Results obtained with the electric vector at  $\pm 45^\circ$  to *a* (within the *ac* plane) are also indicated in Table I. The two spectra obtained with the electric vector at  $\pm 45^\circ$  to *b* (while perpendicular to *a*) were identical, as required by the monoclinic symmetry. (Otherwise these spectra have little immediate significance because of the complicated manner in which the radiation beam is split into *ac* and *b* components).

Four doublets arising from factor-group modes of the Bunn-type (10) orthorhombic hydrocarbon subcells (space group  $D_{2h}^{16}-P_{2121}$ ) are easily identified by comparison with polyethylene spectra (12,13). In terms of subcell symmetry they can be described as  $B_{1u}$  and  $B_{2u}$  components of  $\text{CH}_2$  in-phase stretching, out-of-phase stretching, bending and rocking modes. The frequencies are very close to corresponding polyethylene bands and the polarization is in agreement with the concept of orthorhombic sub-cells built into a monoclinic over-all structure (8). Three weak bands at 761, 782, and 810  $\text{cm}^{-1}$  are assigned to the  $\text{CH}_2$  rocking progression, and eight weak to medium bands from 1197 to 1332  $\text{cm}^{-1}$  to the  $\text{CH}_2$  wagging progression by analogy with related molecules (1-3). The doublets of these bands could not be resolved.

The methyl ester end-groups are arranged in groups of four around  $C_i$  sites of symmetry (8). If inter-

action between consecutive layers of end-groups is neglected (they are separated by chains of  $2 \times 17$  carbon atoms), each molecular ester group mode should give rise to infrared active  $a_u$  and  $b_u$  components, polarized along the  $b$  axis and within the  $ac$  plane, respectively. The relative intensity of the two branches should reflect the orientation of these groups relative to the  $ac$  plane. The C=O stretching mode, two C-O stretching modes and the COC angle bending mode are assigned by analogy with related molecules (14,15) as indicated in Table I. The higher C-O stretching mode is most probably coupled with  $\text{CH}_2$  wagging modes, the lower one with skeletal CC modes (15). It is interesting to note, nevertheless, that the bands associated primarily with the COC grouping (1177, 987, 700  $\text{cm}^{-1}$ ) have very weak components along the  $b$  axis, in agreement with the known orientation of the COC angles with respect to the  $ac$  plane (8). The frequencies of the very weak  $a_u$  branches could not be determined with any precision, but the splitting between  $a_u$ ,  $b_u$  branches appears to be very small. The C=O stretching band (1742  $\text{cm}^{-1}$ ) has a strong  $b_u$  component and weaker  $a_u$  component, again in agreement with the known structure. Some remaining bands can be associated with well-known characteristic modes of  $\text{CH}_3$  groups and  $\alpha$   $\text{CH}_2$  groups (14), as indicated in Table I. A few weak bands remain unassigned.

The observed infrared anisotropy, as discussed, is in general agreement with the assignments and with the known structure (8); i.e., with the monoclinic overall symmetry, tilted hydrocarbon chains, orthorhombic sub-cell packing (describing the repetition in and of the hydrocarbon chains), and the orientation of the ester groups relative to the  $ac$  plane. In view of the fact that some of the discussed modes are "group vibrations" only in a very broad sense, the agreement with simple predictions appears to be better than expected.

#### Methyl 1-Octadecyl Sulfonate

The crystal structure of this compound (or any closely related homologue) does not appear to have been reported. Figure 2 shows spectra obtained with perpendicular incidence and the electric vector along mutually perpendicular directions designed  $a$  and  $b$  ( $a$  parallel to crystal growth). The spectra obtained with the electric vector at  $\pm 45^\circ$  to  $b$  (while perpendicular to  $a$ ) were identical, suggesting monoclinic symmetry. The two spectra obtained with the electric vector at  $\pm 45^\circ$  to  $a$  (while perpendicular to  $b$ ) were quite different and indicated tilted hydrocarbon chains. The frequencies of prominent absorption bands and their polarization is given in Table II.

It is immediately obvious that the polarization of bands arising from  $\text{CH}_2$  modes is quite different from methyl stearate. The symmetric stretching mode (2848  $\text{cm}^{-1}$ ) and the bending mode (1463  $\text{cm}^{-1}$ ) have strong  $b$  components only, while the antisymmetric stretching mode (2923  $\text{cm}^{-1}$ ) has a strong  $ac$  component. The  $\text{CH}_2$  rocking band is obscured by a band associated with sulfonate groups (see below). The  $\text{CH}_2$  stretching region is complicated by a band polarized along the  $b$  axis and observed very close to the antisymmetric  $\text{CH}_2$  stretching band. It can be assigned to a combination band involving Raman active  $\text{CH}_2$  bending modes (11). The frequencies and polarization of all observed  $\text{CH}_2$  modes is very similar to triclinic  $n\text{-C}_{20}\text{H}_{42}$  (11) and to form  $A'$  carboxylic acids (3), leading to the conclusion that the zigzag

TABLE II  
Polarized Infrared Spectrum of Methyl 1-Octadecyl Sulfonate  
[ $\text{CH}_3(\text{CH}_2)_{17}\text{SO}_3\text{CH}_3$ ]

$\text{cm}^{-1}$	Int.	Pol.	Assignment	
2923	s	ac $\perp$	$\text{CH}_2$ a.s.	
2920	s	b	$\text{CH}_2$ b.(R) + $\text{CH}_2$ b.(I.R.) <sup>a</sup>	
2848	s	b	$\text{CH}_2$ s.s.	
1468	w	ac $\parallel$	( $\text{OCH}_3$ b.)	
1463	s	b	$\text{CH}_2$ b.	
1410	w	b	$\alpha$ $\text{CH}_2$ b.	
1357	s	ac ( $\perp$ to a)	} $\text{SO}_2$ a.s.	
1341	vs	b		
1312	}	w	ac $\parallel$	} $\text{OH}_2$ w.
1296				
1279				
1262				
1245				
1228				
1208				
1188				
1176				
1158				
998	s	ac $\perp$	C-O (S-O) s.	
826	m	ac ( $\perp$ to a)	} S-O (C-O) s.	
822	s	b		
725	m	ac $\perp$	} C-S s. and $\text{CH}_2$ r.	
721	m	b		
580	s	b,ac	(C-SO <sub>2</sub> -O-C skel.)	
524	m	ac	$\text{SO}_2$ b.	
466	m	b,ac	} (C-SO <sub>2</sub> -O-C skel.)	
430	s	b,ac		

Abbreviations and symbols as in Table I.

<sup>a</sup> Combination involving Raman active mode (11).

planes are all essentially parallel to each other and roughly perpendicular to the  $ac$  plane.

The sulfonate groups (C-SO<sub>2</sub>-O-C) should give rise to twelve skeletal modes which could be approximately described as follows: three  $\text{SO}_2$  internal modes (sym. st., asym. st., bend.); three  $\text{SO}_2$  modes of rotatory origin (wagging, twisting, rocking); six CSOC chain-modes (three stretching, two angle-bending, one torsional mode). Nine medium to strong bands evidently not associated with hydrocarbon chains are observed between 400 and 1400  $\text{cm}^{-1}$ . The  $\text{SO}_2$  stretching modes give rise to well-known group frequencies (14) and are easily located. The  $\text{SO}_2$  bending mode is assigned to the 524  $\text{cm}^{-1}$  band, which shows the same polarization as the symmetric stretching mode and occurs in the expected frequency range (14,17,18). Three prominent bands between 700 and 1000  $\text{cm}^{-1}$  are assigned to stretching modes of the CSOC grouping by comparison with low molecular weight alkyl sulfonates (18). These modes are probably strongly coupled. The qualitative descriptions in Table II are based on the general observation that C-O stretching modes usually absorb in the vicinity of 1000  $\text{cm}^{-1}$ , CS modes around 700  $\text{cm}^{-1}$  (14). (In dilute solution the 725 and 826  $\text{cm}^{-1}$  bands split into a total of five distinct bands, reflecting rotational isomerism within the CSOC grouping). Three remaining medium to strong bands between 400 and 600  $\text{cm}^{-1}$  are probably associated with rotatory  $\text{SO}_2$  modes and skeletal bending modes. A more detailed assignment does not appear possible at present.

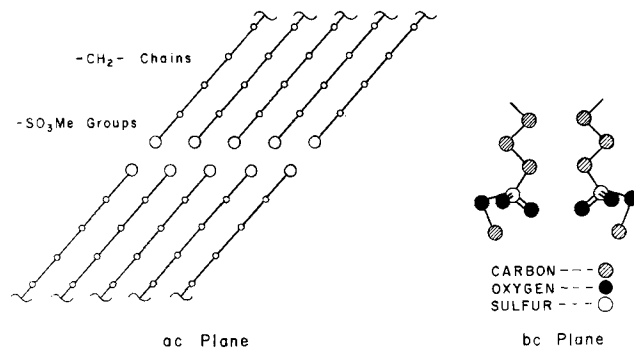


FIG. 3. Proposed schematic structure of methyl 1-octadecyl sulfonate.

The relative intensities of the *b* and *ac* components of "internal" SO<sub>2</sub> modes lead to qualitative conclusions regarding the structure and packing of the C-SO<sub>2</sub>-O-C groupings. (The form of the remaining modes cannot be described in much detail and their polarization is therefore of less immediate significance.) As shown in Figure 2, the symmetric SO<sub>2</sub> stretching (1158 cm<sup>-1</sup>) and the bending mode (524 cm<sup>-1</sup>) have very weak *b* components, while the antisymmetric stretching mode has a strong *b* component (1341 cm<sup>-1</sup>) (For corresponding CH<sub>2</sub> modes the reverse is true.) The polarization of these three SO<sub>2</sub> modes is thus internally consistent and suggests that the bisectors of all SO<sub>2</sub> groups are approximately parallel to the *ac* plane.

In Figure 3 the structural conclusions are presented in a schematic way. The polarization of the bands assigned to S-O and C-O stretching modes is in qualitative agreement with the proposed arrangement of the molecules, although their description as localized bond-stretching vibrations must be regarded as approximate.

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[Received March 14, 1966]