

The Infrared Spectra and Polymorphism of Long Chain Esters: IV. Some Esters From Tetradecanol, Hexadecanol, Octadecanol, Eicosanol, Docosanol and Dodecanoic, Tetradecanoic, Hexadecanoic, Octadecanoic and Eicosanoic Acid¹

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ABSTRACT

Infrared spectra and x-ray diffraction photographs have been recorded for some normal-chain esters of long chain acids and long chain alcohols. The substances show no polymorphism but two different structure types exist, one with the chains tilting towards the end group planes and one with vertical chains. The IR spectra permit determination of the chain length of the acid methylene chain. The length of the alcohol chain cannot be deduced.

INTRODUCTION

As a continuation of a program of studying fatty acid esters some wax esters have been investigated. In the earlier parts of this series (1-3) some groups of long chain esters were found to be polymorphic. It was also found that the IR spectra differed considerably between esters with long acid part and long alcohol part. A review of the field and details of the experimental technique are found in Reference 4.

Some x-ray studies on wax esters are reported in the literature. Kreger and Schamhart (5) prepared some of these esters and determined their melting points and long-spacings. By comparing the latter with calculated values they decided that, among others, octadecyl hexadecanoate crystallized in a form with vertical chains, i.e., perpendicular to the end group planes, while most others crystallized in a tilted form. Tetradecyl octadecanoate and docosyl octadecanoate gave spacings for both types of form. It was concluded that the appearance of the vertical form was a feature inherent in some of the esters and not caused by impurities.

¹Parts I, II and III of this series have appeared in *Arkiv Kemi* 31:267, 283, 291 (1969).

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Lutz et al. (6) accurately determined the long-spacings of several wax esters. Crystals of tetradecyl tetradecanoate, tetradecyl hexadecanoate, hexadecyl hexadecanoate, octadecyl tetradecanoate, hexadecyl octadecanoate and octadecyl octadecanoate were considered to be isomorphous and also isomorphous with crystals of ethyl esters of long acids. The powder patterns could be indexed on the basis of the unit cell of hexadecyl hexadecanoate as given by Kohlhaas (7). Hexadecyl tetradecanoate, tetradecyl octadecanoate and octadecyl hexadecanoate were found to have another form with the chain axis almost vertical. Esters of some alcohols with an odd number of carbon atoms gave several sets of long-spacing lines indicating the existence of polymorphs.

A number of studies of the dielectric absorption of the wax esters have been reported (8-12).

Iyengar and Schlenk (13) have prepared a number of the wax esters and determined their melting points. When these were plotted against the difference in the number of carbon atoms in the alcohol and the acid chains as in Figure 1, there was a striking deviation from regularity for the difference +2 in that the melting points were higher than interpolation would predict. This group of compounds includes some of those which had been claimed to have vertical chains by the earlier workers. It was considered worth while by the present authors to extend the study of the available wax esters.

EXPERIMENTAL PROCEDURES

The substances synthesized by Iyengar and Schlenk (13) have a purity of 99% or better as shown by thin layer chromatography (TLC) and gas chromatography (GLC). The melting points in Figure 1 had been determined on a Kofler Micro Hot Stage using a heating rate of 1-2 C/min. They have also been determined in a Mettler FP2 apparatus with a rate of 0.2 C/min.

The values obtained were generally lower, on the average 0.8 C.

Powder photographs have been recorded with a Guinier type camera and also during continuously varying temperature in a so-called DPT camera (Diffraction Pattern-Temperature) described by Stenhagen (14).

IR spectra have been recorded with a Perkin-Elmer Model 157 spectrophotometer. The substances were mixed with freeze-dried potassium bromide in an agate mortar and pressed to pellets with cold tools. This gentle mixing avoids destruction of the sample crystals, known to occur by prolonged treatment of samples with crystalline potassium bromide in vibration mills. With the present kind of pellet preparation, the crystal form is not altered as shown by a comparison of potassium bromide and Nujol mull spectra of polymorphic long chain fatty acids (15). During the first recording, the temperature in the pellet was kept at about 25 C by air cooling. In many cases spectra have also been recorded at higher temperatures and after melting and cooling. The instrument is linear in wavelength, but in the text wave numbers will be used. According to the specification, the accuracy in wave numbers is $\pm 2 \text{ cm}^{-1}$ and the resolution 5 cm^{-1} at 1000 cm^{-1} .

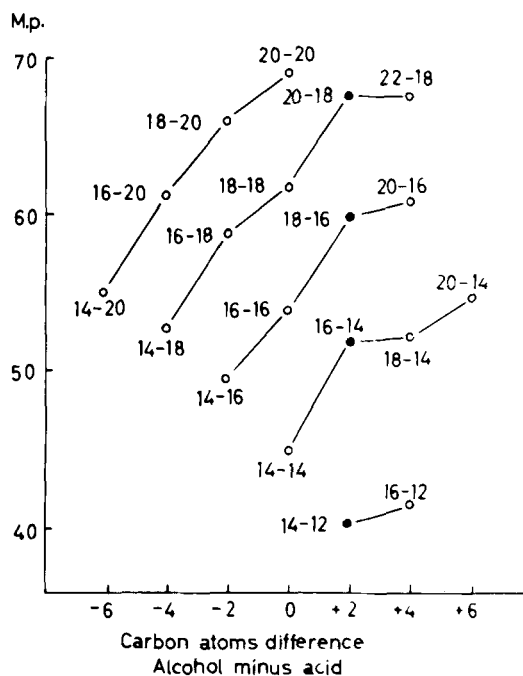


FIG. 1. Melting points of saturated wax esters (13). The figures denote the number of carbon atoms in the alcohol and acid part respectively.

X-RAY STUDIES

The Guinier photographs showed side spacings characteristic of β -forms according to the nomenclature of Larsson (16). This was confirmed by the IR spectra and means that the chain packing is of the orthorhombic type with every other chain plane almost perpendicular to the others. Due to strong orientation effects in the specimens, no long-spacing lines were obtained.

The DPT photographs showed no phase transitions during heating. The phase crystallized from melt always showed the same long-spacing as the original solvent-crystallized specimens. The intensities of the lines could differ much for specimens differently solidified, but this difference is probably caused by orientation effects, and it thus seems that all the substances occur in only one form. This was also the case for esters of even alcohols investigated by Lutz et al. (6).

The values of long-spacings obtained with the DPT camera are not so accurate as those of Lutz and coworkers. For the nine substances common to both studies the greatest deviation

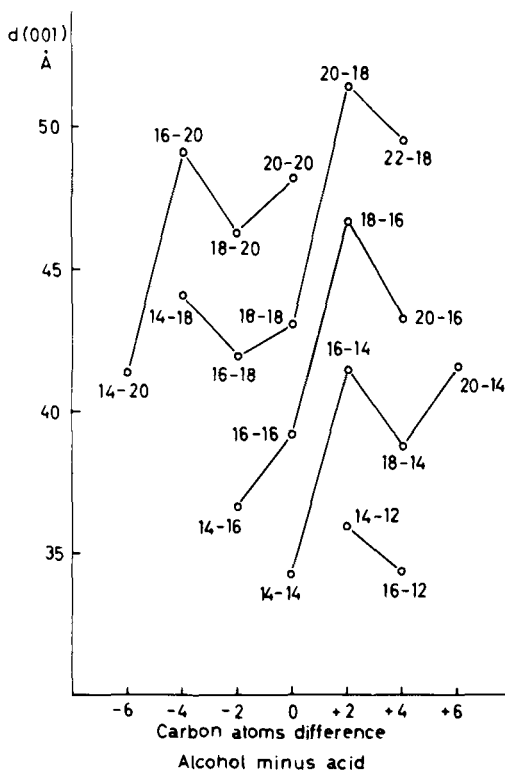


FIG. 2. Long-spacings of saturated wax esters. The figures denote the number of carbon atoms in the alcohol and acid part respectively.

TABLE I

Long-spacings (A) of Wax Esters

Ester	Type ^a	Present study	Reference 6	Reference 5 ^b
Tetradecyl dodecanoate	V	36.0		
Hexadecyl dodecanoate	T	34.4		
Tetradecyl tetradecanoate	T	34.3	34.54 ± 0.06	
Hexadecyl tetradecanoate	V	41.5	41.36 ± 0.04	
Octadecyl tetradecanoate	T	38.8	38.98 ± 0.02	
Eicosyl tetradecanoate	T	41.6		
Tetradecyl hexadecanoate	T	36.7	36.79 ± 0.01	37.0
Hexadecyl hexadecanoate	T	39.2	38.90 ± 0.01	41.2
Octadecyl hexadecanoate	V	46.7	45.98 ± 0.01	40.7
Eicosyl hexadecanoate	T	43.3		46.1
Tetradecyl octadecanoate	V	44.1	43.44 ± 0.01	43.5 (39.3)
Hexadecyl octadecanoate	T	42.0	41.34 ± 0.02	41.4
Octadecyl octadecanoate	T	43.1	43.47 ± 0.02	41.8
Eicosyl octadecanoate	V	51.4		43.7
Docosyl octadecanoate	T	49.5		50.2 (53.9)
Tetradecyl eicosanoate	T	41.4		54.3 (50.7)
Hexadecyl eicosanoate	V	49.1		
Octadecyl eicosanoate	T	46.3		
Eicosyl eicosanoate	T	48.2		

^aV, vertical; T, tilted.

^bValues in parenthesis denote a second set of (weaker) long-spacing lines. Values in two rows denote different preparations.

is 0.7 Å. Our values are given in Table I together with those of Kreger and Schamhart (5) and Lutz et al. (6). When our values are plotted against the carbon atom difference as in Figure 1 the diagram in Figure 2 is obtained. For the difference +2 the same kind of deviation is visible as in the melting point diagram but there is also a longer long-spacing for the difference -4. The latter feature has no counterpart in the melting point diagram in Figure 1.

When comparing the observed long-spacings with values calculated for straight molecules one finds that those with the longer spacings are of the vertical type (marked with V in Table I) while the others are tilted (marked with T in Table I). If the molecules are supposed to be straight also in this phase, the angle of tilt is close to the value 63° found for other esters (17-19).

INFRARED SPECTRA

The spectra have been recorded from 4000 to 700 cm⁻¹, and the interval 1500 to 700 cm⁻¹ is presented in Figures 3-7, in each of which the acid part is the same. In Figure 8 the spectra of the palmityl esters are shown to illustrate the

effect of varying the acid chain length.

The bands in the spectrum of methyl octadecanoate have been assigned to vibrations extensively by Susi and Jahn (20) from measurements with polarized light and the spectrum has also been discussed in connection with the spectra of the homologous methyl alkanoates (21).

The assignment of the bands in methyl octadecanoate is as follows (wave numbers from Reference 20). The antisymmetric stretching of the methylene groups gives rise to a band at 2925/2920 cm⁻¹ while the symmetric stretching appears at 2853/2850 cm⁻¹. The average values obtained for the wax esters are 2914 and 2852 cm⁻¹, respectively. The carbonyl stretching frequency (1742 cm⁻¹) is found at 1731 cm⁻¹. The methylene bending mode (1474/1464 cm⁻¹) is obtained at 1466 cm⁻¹, in some cases with an inflection on the high frequency side. The α-CH₂ bending (1413 cm⁻¹) has been found at 1414 cm⁻¹. The symmetric methyl bending frequency (1380 cm⁻¹) absorbs at 1398 or 1375 cm⁻¹. The latter band has possibly the highest contribution of methyl bending as it disturbs the regular progression pattern.

The band progression caused by the methylene wagging modes (23,24) between about 1380 and 1170 cm^{-1} has been observed to be independent of the length of the alcohol chain in accordance with References 2 and 3. The number of strong peaks between 1330 and 1170 cm^{-1} are for the dodecanoates 6, tetradecanoates 7, hexadecanoates 8, octadecanoates 9 and eicosanoates 10. This is clearly demonstrated in Figure 8. Towards higher wavenumbers two groups of weaker bands appear, the first at 1415 and 1398 cm^{-1} , the second at about 1375 and 1362 cm^{-1} . The latter group is surrounded with more inflections in the longer chain compounds than in the shorter ones. The band at 1375 cm^{-1} is the most intensive one, and probably methyl symmetric bending makes a large contribution to it.

In the region 1150 to 950 cm^{-1} where the C-C stretching vibrations absorb, the spectra show differences both within the series shown in Figures 3-7 and between the series. Here, obviously, the O-alkyl chain has an influence on the spectra. One band around 1099 cm^{-1} and two strong bands at 961 cm^{-1} and 922 cm^{-1} are found in all spectra. They are quite strong and thus probably due to C-C stretching near the ester group or O-CH₂ stretching. O-CH₂ stretching was found by normal coordinate analysis to absorb in that region (846 cm^{-1}) (25). These bands are also prominent in the higher members of the series of octadecanoates described in Reference 2.

A band constant for all spectra is found at 891 cm^{-1} , possibly caused by methyl rocking vibrations. A corresponding band was reported for methyl to octyl stearate (2) where also a band at 879 cm^{-1} occurs. Between about 820 and 740 cm^{-1} there are some weak peaks or inflections caused by methylene rocking vibration. Their positions differ between the series and are the same within the series. In some spectra an extra peak or inflection was observed without any evident relation to chain length. At 730 and 720 cm^{-1} are the two strong methylene rocking peaks characteristic of the chain packings with two sets of nearly perpendicular chain planes [β' -forms according to Larsson (16)].

DISCUSSION

Present studies support the conclusion that in series of wax esters the occurrence of abnormally high melting points--when alkyl is 2 carbons longer than acyl (+2 type)--is correlated with the occurrence of vertical crystal forms. However, esters with the alcohol chain 4 carbon atoms shorter than the acid chain (-4 type) also

are vertical but they do not show high melting points. The vertical phase here seems to have about the same stability as the tilted, and Kreger and Schamhart (5) found both forms for tetradecyl octadecanoate.

A comparison with dielectric data in References 8-12 shows no correlation between the occurrence of rotation and vertical crystal forms. The latter are obviously not of α -type (in which the molecules have considerable orientational freedom around the long axis). This is also in accordance with the x-ray and IR data which in all cases indicate β' -forms.

It is interesting to note that in some cases the dielectric studies (8,9) show transitions between rotating and nonrotating forms. The rotating form often supercools. On heating, the transitions are sharp. The dielectric behavior also depends on the freezing rate. The x-ray studies showed no change in pattern which could be correlated with reported rotational transitions.

The IR spectra show no obvious differences between vertical and tilted forms or between rotating and nonrotating forms. This may be taken as a confirmation of the view expressed by Crowe and Smyth (8) and Hunter and Eddy (12) that the molecules rotate as a whole so that the molecular geometry is not changed and does not cause marked changes in the IR spectra.

For most substances the spectra have been recorded also during cooling of the melted specimen. As judged from the appearance of the 720 cm^{-1} region a β' -form (with a double peak) is formed directly from the melt.

Tetradecyl octadecanoate, however, showed a spectrum with a single peak at 720 cm^{-1} while the rest of the spectrum (recorded earlier) indicated a solid substance. The DPT photographs showed no changes below the freezing point. The substance was found to be nonrotating by Crowe and Smyth (8) and Crowe et al. (9) and their curves indicate no transition. An explanation might be that solidification is not a simple process in that each individual molecule could be in the same all-*trans* configuration as in the solid, thereby giving mostly the same spectrum as solid, but that the chain packing is not yet ordered in the orthorhombic way necessary for giving a doublet at 720 cm^{-1} . More detailed experiments with accurate temperature control are needed to clarify the situation.

The IR spectra give information as to the chain length of the acid part, in that the number of progression bands between about 1330 and 1170 cm^{-1} is half the number of carbon atoms in the acid. The O-alkyl chain modes are obviously not intensified in the same

way as those of the C-bonded chain, and changes in the length of the alcohol chain make only small differences in the spectra, mainly in the region of skeletal vibrations at 1150 to 950 cm^{-1} . From the appearance of this region and the number of progression bands between 1330 and 1170 cm^{-1} it should be possible to identify these wax esters when reference spectra are available.

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