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# A New Crystal Form of Fatty Acids*

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An investigation of the infrared spectra of single crystals of hexadecanoic, octadecanoic and docosanoic acids has provided evidence for the existence of a new crystal form. In the present paper the infrared spectrum of the new form of hexadecanoic acid is compared with the spectra of the *A*-, *B*- and *C*-forms. Some conclusions about the structure of the new form are presented.

## Introduction

The fatty acids crystallize in a variety of forms. Thus, two triclinic and two monoclinic forms are known for several normal carboxylic acids with an even number of carbon atoms (von Sydow, 1956*a*). In a recent investigation of the infrared spectra of single crystals of fatty acids we have obtained evidence for the existence of a new crystal form of hexadecanoic, octadecanoic and docosanoic acids. The evidence has been presented in detail for octadecanoic acid (Holland & Nielsen, 1962*b*). In the present paper the infrared spectrum of the new form of hexadecanoic acid will be presented and compared with the spectra of the previously known *A*-, *B*-, and *C*-forms. It is hoped that the existence of the new crystal form may soon be confirmed by X-ray diffraction studies and that its structure may be determined in detail.

## Infrared spectra of four forms of hexadecanoic acid

Triclinic crystals of hexadecanoic acid were grown by evaporating a carbon disulfide solution at −9 °C. They appeared as thin sheets with irregular edges marked by parallel lines similar to those observed in triclinic crystals of octadecane (Holland & Nielsen, 1962*a*) and octadecanoic acid (Holland & Nielsen, 1962*b*). This indicates that they have the standard *A*-form rather than the superstructure described by von Sydow (1956*a*, *b*). However, an attempt to verify this by comparing their infrared spectrum with the partial spectrum of polycrystalline triclinic hexadecanoic acid in a Nujol mull published by von Sydow (1955*a*) proved inconclusive.

A small crystal was mounted on the stage of a reflecting microscope attached to a Perkin–Elmer Model 112 infrared spectrometer in such a manner that the linearly polarized radiation was incident normal to the large crystal face. A single strong band, caused by methylene rocking, was observed at 718 $\text{cm}^{-1}$. Its intensity varied as the crystal was rotated about the normal. The spectrum obtained with the crystal rotated so as to make this band a maximum is represented by the broken transmission curve in Fig. 1. The crystal was then rotated 90° about the normal, and the spectrum shown by the solid curve was obtained.

Both the strong methylene rocking band at 718 $\text{cm}^{-1}$ and the methylene deformation band at 1468 $\text{cm}^{-1}$ should be polarized perpendicular to the chain axis. The change in dipole moment for the rocking vibration should be perpendicular to the chain skeletal plane, while that for the methylene deformation, or 'scissoring', should be parallel to the skeletal plane. Since both of these bands are observed with high intensity in Fig. 1, the former only in the broken curve and the latter in the solid curve, it was assumed that the incident radiation makes a fairly small angle with the chain axes and that the two transmission curves differentiate between bands polarized, respectively, perpendicular and parallel to the planes of the carbon atoms in the methylene chains.

The interpretation of the spectrum, which follows readily from the work on octadecanoic acid (Holland & Nielsen, 1962*b*), will not be given in detail here, but the assignment of some of the bands, in addition to the $CH_2$ rocking and deformation modes at 718 and 1468 $\text{cm}^{-1}$, respectively, will be briefly stated. The bands between 1186 and 1350 $\text{cm}^{-1}$ are caused largely by $CH_2$ wagging, coupled with and intensified by carboxyl vibrations. The band at 1407 $\text{cm}^{-1}$ is ascribed to deformation of the $CH_2$ groups adjacent to carboxyl groups. The bands between 1000 and 1150 $\text{cm}^{-1}$ are caused largely by deformations of the carbon skeleton. The band at 1369 $\text{cm}^{-1}$ is ascribed to symmetrical deformation of the methyl end-groups, and those near 677, 880, 1440 and 1690 $\text{cm}^{-1}$ are caused by vibrations of the carboxyl groups.

The fact that the bands at 718 and 1468 $\text{cm}^{-1}$ appear to be single, and not split into two or more components, might be taken to indicate that the crystal has the standard *A*-form with only one dimer per unit cell. However, since both *A*-forms have the same triclinic chain subcell, there should be no

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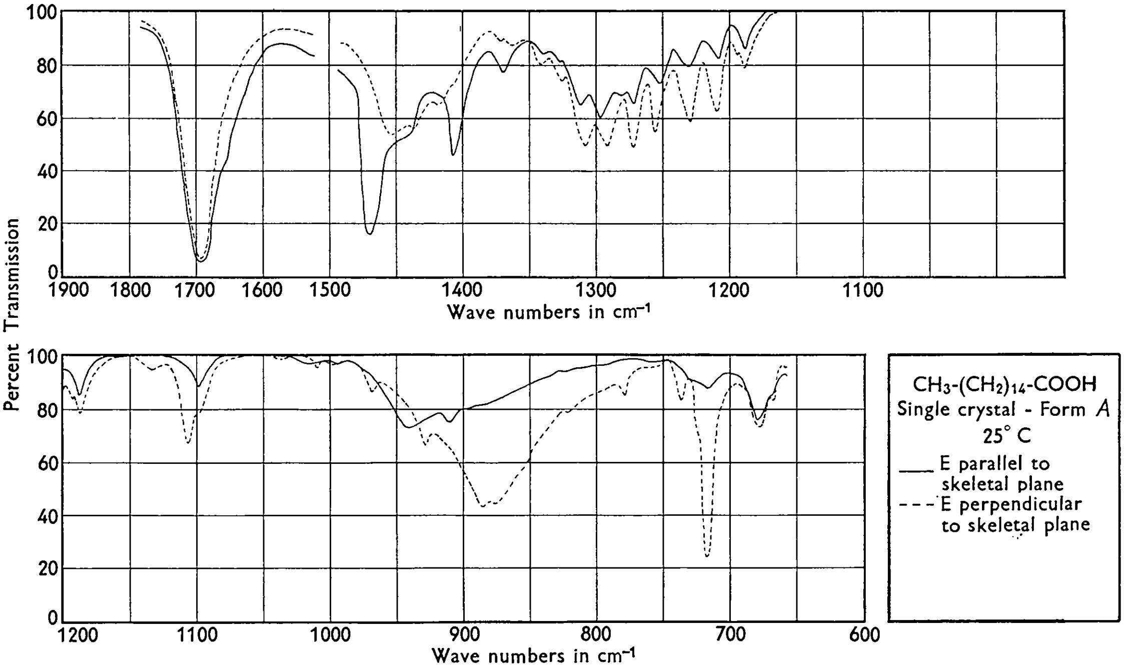

Fig. 1. Infrared spectrum of a single *A*-form crystal of hexadecanoic acid. Linearly polarized radiation incident approximately parallel to the chain axes.

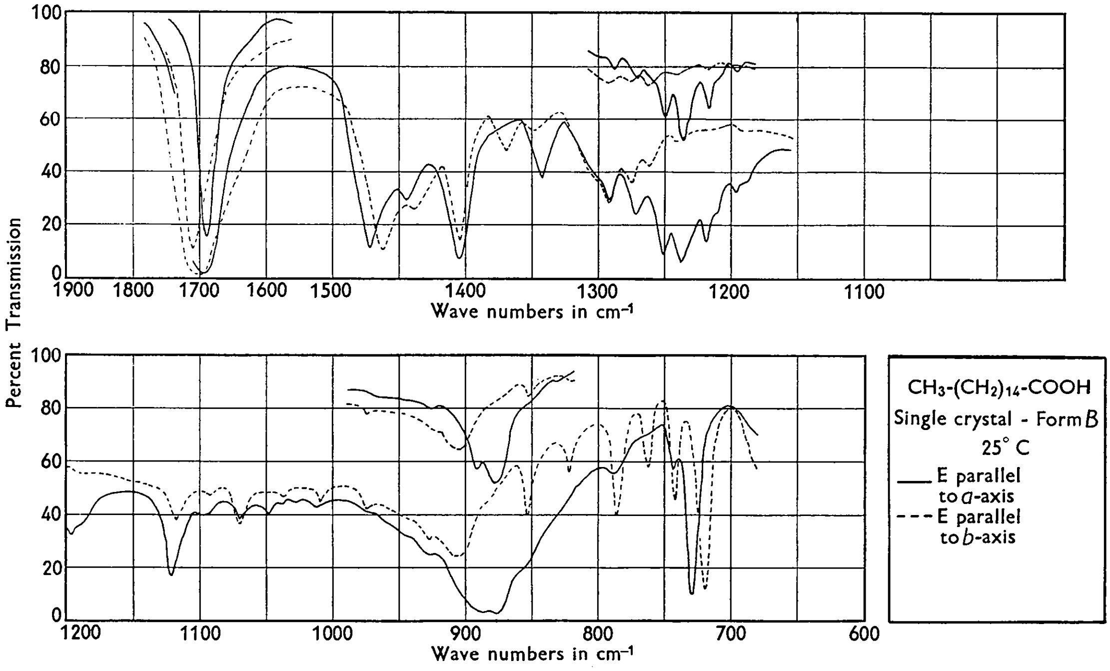

Fig. 2. Infrared spectum of a single *B*-form crystal of hexadecanoic acid. Linearly polarized radiation incident normal to the *ab*-planes.

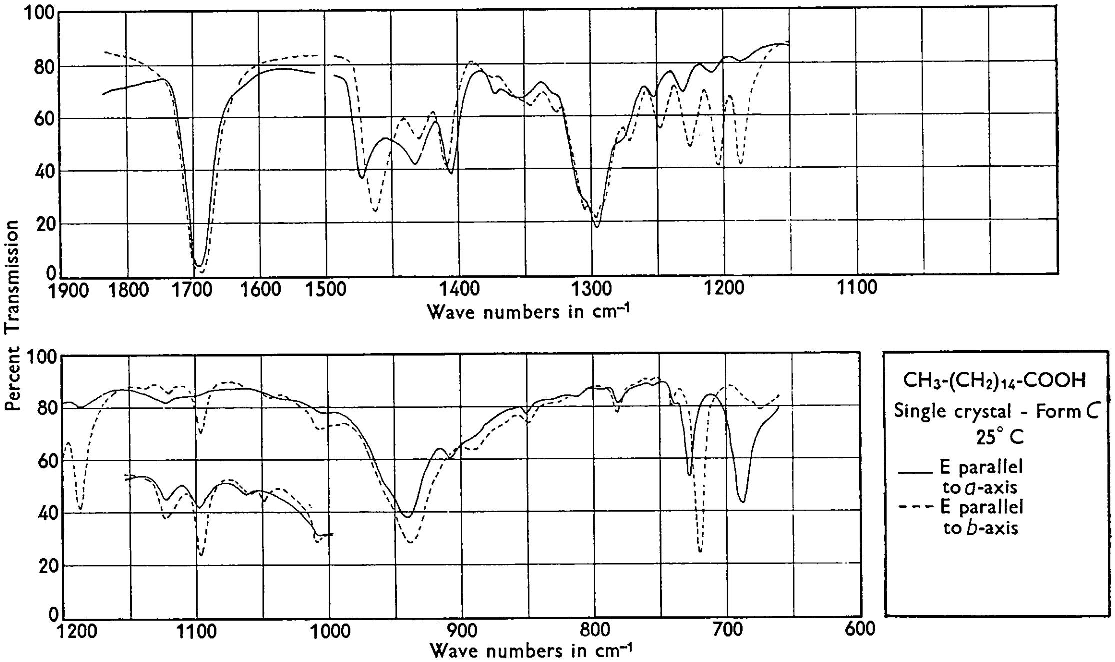

Fig. 3. Infrared spectrum of a single *C*-form crystal of hexadecanoic acid. Linearly polarized radiation incident normal to the *ab*-planes.

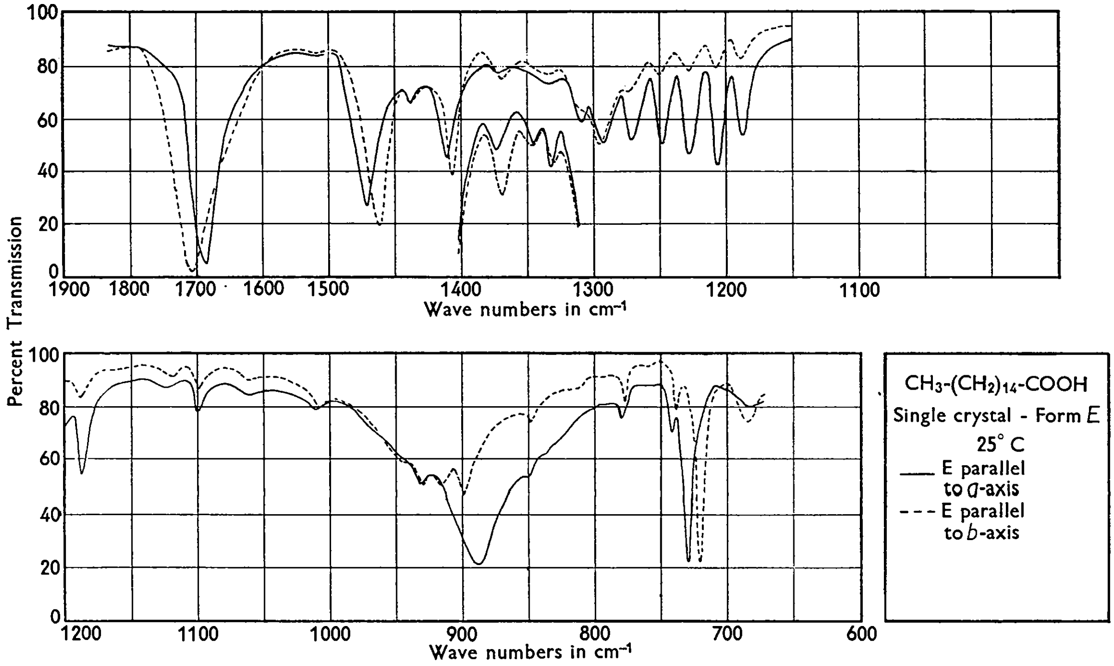

Fig. 4. Infrared spectrum of a single crystal of the new form ('*E*-form') of hexadecanoic acid. Linearly polarized radiation incident normal to the *ab*-planes.

splitting of the methylene vibrations in either form.

*B*-form crystals of hexadecanoic acid were grown by evaporating a carbon disulfide solution at 18 °C. These monoclinic crystals are lozenge-shaped with an acute interedge angle of 74°. The crystallographic axis parallel to the bisector of the acute interedge angle will here be denoted by '*a*', and the axis perpendicular to this bisector will be denoted by '*b*'. This convention, which is the reverse of that used by von Sydow (1955*b*) was used in a previous paper on octadecanoic acid (Holland & Nielsen, 1962*b*) because it resembles the convention used for normal paraffins. The *c*-axis is tilted toward the *b*-axis, making an angle of 27° 22′ with the normal to the *ab*-plane (von Sydow, 1955*b*). The unit cell group is isomorphic to the point group $C_{2h}$. The unit cell contains two dimers. The methylene chains are very nearly parallel to the *c*-axis.

The infrared spectrum of a single *B*-form crystal is shown in Fig. 2. The linearly polarized infrared radiation was parallel to the normal to the *ab*-planes. The solid percent transmission curve was obtained with the electric field in the incident radiation parallel to the *a*-axis, and the broken curve was obtained with the field parallel to the *b*-axis. It will be noticed that the strong methylene rocking and deformation bands are split into two differently polarized components separated by 10 cm$^{-1}$. Many of the other bands are also split, but for most of them the separation between components is considerably smaller. This splitting results from coupling between the vibrations of the two dimers in the unit cell (Stein & Sutherland, 1954; Stein, 1955). In addition to this splitting, there are other striking differences between the spectra of the *B*- and *A*-form crystals. Thus the appearance of the bands in the region from 1150 to 1350 cm$^{-1}$ is quite different in the two spectra.

*C*-form crystals of hexadecanoic acid were obtained by evaporating an isopropyl ether solution at 27 °C. These monoclinic crystals are lozenge-shaped with an acute interedge angle of 55°. The *c*-axis is tilted toward the *a*-axis, and the tilt is nearly 39° (Abrahamsson & von Sydow, 1954). The unit cell contains two dimers. The infrared spectrum of such a crystal is shown in Fig. 3. The radiation was incident normal to the *ab*-planes. The solid curve was obtained with the electric vector parallel to the *a*-axis, and the broken curve with the electric vector parallel to the *b*-axis.

The splitting of the strong methylene rocking and deformation bands is about as in the *B*-form, but otherwise the spectrum is quite different from that of the *B*-form, as well as from that of the *A*-form. Thus, the strong carboxyl bands, which lie at about 880 and 1240 cm$^{-1}$ in the *B*-form, have shifted to 940 and 1300 cm$^{-1}$ in the *C*-form. Also, the splitting of the carbonyl band near 1700 cm$^{-1}$ is almost absent in the *C*-form and the polarizations of the components have been reversed. These and other differences between the infrared spectra of the *B*- and *C*-form fatty acid crystals have been explained as resulting from the differences in the direction and amount of the tilt of the *c*-axis and in the molecular configuration (Holland & Nielsen, 1962*b*).

The new crystal form was first observed for octadecanoic acid. When an ether solution of this acid was evaporated at 18 °C most of the crystals in the residue had the *C*-form with the acute interedge angle of 55°. However, some crystals with the interedge angle of 74° were also present. These were first assumed to have the *B*-form, and little attention was paid to them, since good *B*-form crystals had already been grown from a carbon disulfide solution. Later, after deuterated octadecanoic acid, $CH_3\text{–}(CH_2)_{16}\text{–}COOD$, had been prepared, a solution of this acid in ethyl ether was evaporated at 9 °C in an effort to grow crystals of the *B*-form. Some crystals with an interedge angle of 74° were produced. However, although their spectrum showed some similarity to that of the *B*-form of the ordinary acid, differences were observed that seemed too great to be accounted for by the deuteration. Attention was then directed to the crystals of the ordinary acid with an interedge angle of 74° which had been precipitated from the ether solution along with crystals of the *C*-form. The spectrum of one of these crystals was obtained. It turned out to be different from that of the *B*-form and also quite unlike those of the *A*- and *C*-forms. Thus, it seemed certain that this crystal had a structure different from that of any of the known polymorphs of octadecanoic acid. Since the letter *D* has been associated with the crystal form of odd-numbered fatty acids (Francis, Piper & Malkin, 1930), the new form was referred to as the *E*-form (Holland & Nielsen, 1962*b*). This designation should be regarded as temporary, pending determination of the long spacing.

After it had been recognized that octadecanoic acid crystals having an interedge angle of 74° may have one or another of two different forms a number of crystals grown previously were examined. It was found that a few crystals of the *E*-form are usually produced when *B*-form crystals are grown. When a solution of octadecanoic acid in ethyl ether is evaporated at 0 °C all the crystals grown apparently have the *E*-form, although some are not lozenge-shaped but appear as long thin ribbons.

*E*-form crystals of hexadecanoic acid were grown in the same manner as such crystals of octadecanoic acid. Attempts to produce *B*-form crystals of docosanoic acid by evaporation of a carbon disulfide solution at 25 °C yielded only crystals of the *E*-form.

The infrared spectra of the *E*-form of ordinary and deuterated octadecanoic acid have been presented and interpreted elsewhere (Holland & Nielsen, 1962*b*). The spectrum of a single *E*-form crystal of hexadecanoic acid is shown in Fig. 4. The lozenge-shaped crystal was mounted so that the linearly polarized radiation was incident normal to the large crystal surface. The solid and broken transmission curves were obtained with the electric vector parallel to the bisectors of the acute and obtuse interedge angles, respectively. These directions are presumably those of the *a*- and *b*-axes, as indicated in the legend.

The splitting and polarization of the strong bands near 720 and 1465 $\text{cm}^{-1}$, caused by methylene rocking and deformation, respectively, indicate that the chains have the orthorhombic packing. The fact that, within the error of the fairly rough measurement, the *E*- and *B*-forms have the same interedge angles indicates that the methylene chains have about the same tilt in the two forms. Hence, these probably differ mainly in the configuration or arrangement of the end-groups. It is possible that the *E*-form has the unusual orthorhombic chain packing found by Abrahamsson (1959*a*, *b*) for 2-D-methyloctadecanoic acid.

The splitting of the band ascribed to symmetrical methyl deformation into components at 1369 and 1373 $\text{cm}^{-1}$ shows that the methyl groups of neighboring molecules are fairly close together. The polarization and intensity of these components indicate that the relative orientation of the methyl groups is similar in the *E*- and *B*-forms.

The C=O stretching doublet near 1700 $\text{cm}^{-1}$, and the broad carboxyl band near 900 $\text{cm}^{-1}$, resemble the corresponding bands of the *B*-form. The splitting indicates that, because of the fairly small chain tilt, the carboxyl groups in neighboring dimers are close enough to interact appreciably, as they are in the *B*-form but not in the *C*-form.

Other parts of the spectrum of the *E*-form differ greatly from the same regions of the spectrum of the *B*-form. Thus, the band at 686 $\text{cm}^{-1}$ has no observed counterpart in the *B*-form. The methylene rocking bands above 730 $\text{cm}^{-1}$ are weaker and lie at slightly lower wave numbers. The series of bands between 1186 and 1350 $\text{cm}^{-1}$ are more regularly spaced than the corresponding bands of the *B*-form.

The spectrum of the new crystal form is also quite different from that of the *C*-form. The latter has a strong carboxyl band at 940 $\text{cm}^{-1}$, while the corresponding band of the *E*-form lies at about 880 $\text{cm}^{-1}$. In the region from 1150 to 1300 $\text{cm}^{-1}$ the bands of the *E*-form lie nearly at the same wave numbers as those of the *C*-form and have nearly the same relative intensities. However, in the *E*-form these bands are stronger when the electric vector in the incident radiation is parallel to the *b*-axis, while in the *C*-form they are stronger when it is parallel to the *a*-axis. This indicates that the chains in the *E*-form are tilted in the same direction as in the *B*-form. A similar difference in polarization is found for the bands near 686 $\text{cm}^{-1}$.

The differences in the regions from 650 to 700 $\text{cm}^{-1}$ and from 1150 to 1350 $\text{cm}^{-1}$ between the spectra of the *B*- and *C*-forms have been attributed to a different orientation of the carboxyl groups with respect to the methylene chains (Holland & Nielsen, 1962*b*). Hence, the similarities between the spectra of the *E*- and *C*-forms in these regions may indicate that the molecular configuration is nearly alike in these forms.

## Concluding remarks

Since fatty acid crystals of the new form are easily grown, they have most likely been observed before. They have not been recognized, since they resemble the *B*-form crystals in appearance, and since the spectra of polycrystalline samples of the *C*- and *E*-forms do not differ greatly.

The features of the structure of the new crystal form which have been tentatively inferred from the infrared spectrum and the shape of the crystals may be summarized as follows:

(1) The molecules are dimeric and their configuration is much as in the *C*-form.

(2) The dimers are arranged in parallel layers parallel to the large surfaces of the lozenge-shaped crystals.

(3) The methylene chains have the orthorhombic packing, and their tilt is similar to that in the *B*-form (and in monoclinic *n*-$C_{36}H_{74}$).

The new form is undoubtedly monoclinic. Since the number of infrared bands in its spectrum seems to be the same as in the spectra of the *B*- and *C*-forms, the dimers probably have an inversion center.

It is to be hoped that these conclusions may soon be tested by X-ray diffraction and that the crystal structure of the new form may be determined in detail.

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