

# INFRARED ANISOTROPY OF TRICLINIC *trans*-8-OCTADECENOIC ACID

BY ANNE S. JAHN AND H. SUSI

Eastern Regional Research Laboratory,<sup>1</sup> Philadelphia, Penna.

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A previous investigation with polarized infrared radiation indicated that crystalline *trans*-11-octadecenoic acid has a more regular structure than any of the known forms of saturated normal fatty acids.<sup>2</sup> The present communication reports the results of a similar study on *trans*-8-octadecenoic acid. Powder diffraction work has shown that in the *trans*-6 through *trans*-12-octadecenoic acids all odd and all even acids have a similar structure but substantial differences exist between the two groups.<sup>3</sup> It became obvious at the beginning of the present investigation that *trans*-8-octadecenoic acid crystallizes in the triclinic system. Application of polarized infrared methods to molecular crystals is complicated by the fact that structurally significant directions are defined inside the absorbing medium, whereas the propagation direction and polarization of the radiation beam is easily identified only outside the medium.<sup>4</sup> Particular care is necessary with triclinic systems and the results must be expected to be of a more qualitative nature than in the case of crystals with higher symmetry.<sup>4,5</sup> Additional experimental work on triclinic crystals should help to evaluate the usefulness and/or limitations of such studies.

## Experimental

The sample has been described.<sup>6</sup> An oriented film between rock-salt plates was prepared by previously discussed methods.<sup>2</sup> A Perkin-Elmer Model 21 instrument equipped with a rock-salt prism and silver chloride polarizer was used. It was not possible to specify the exact orientation of the sample. It was assumed that the layers of the end-groups were parallel to the planes of the sample, as found for previously investigated acids,<sup>2</sup> and parallel to

the *ab* planes as in all known saturated acids.<sup>7</sup> This assumption is supported by the polarization of the OH stretching band which is very similar to form C stearic acid.<sup>2</sup> The band is apparently polarized in a unique direction, which we call *c'*. The projection of *c'* on the plane of the sample is designated *a*, the direction perpendicular to *a* and to *c'* is called *b*. *a*, *b* and *c'* coincide with corresponding directions in Fig. 1 of reference 2. Bold face letters are used to avoid confusion with crystallographic axes. Spectra were first obtained with the electric vector  $\epsilon$  along *a*, *b*, *a'*, *a''*, *b'* and *b''*. (The nomenclature is identical with the one used in earlier work.<sup>2</sup>) Additional data were obtained with perpendicular incidence and the electric vector at 15° increments, parallel to the sample plane. The directions of the electric vector refer to the beam before it enters the sample.

## Results

The spectra obtained with tilted radiation beams revealed no planes or glide planes of symmetry, in contrast to the previously studied *trans*-11 acid and the saturated parent compound, stearic acid.<sup>2</sup> CH<sub>2</sub> rocking and bending bands around 720 and 1470 cm.<sup>-1</sup> were not found to be split and polarized in the manner which is characteristic for orthorhombic hydrocarbon substructure.<sup>2,8</sup> Absence of an in-phase C=O stretching band, known from Raman measurements to occur around 1650 cm.<sup>-1</sup>,<sup>9</sup> suggests centrosymmetric dimers, as in all previously studied carboxylic acids.

These observations indicate that centrosymmetric dimers are packed into a triclinic system in such a way that no orthorhombic hydrocarbon substructure results. The highest possible space group symmetry is C<sub>i</sub><sup>1</sup>-P $\bar{1}$ .

Because of the low over-all and substructure symmetry, the polarization of all the numerous absorption bands is not discussed; nor is a detailed assignment attempted. The spectra observed with  $\epsilon$  along *a* and *b* (perpendicular incidence) and the spectra with  $\epsilon$  approximately parallel or perpendicular to *c'* (within the *ac* plane, nonperpendicular incidence) are shown in Fig. 1. *a*, *b* and *c'* have been defined in the Experimental section. Some qualitative suggestions about the shape and packing of the molecules are made on the basis of splitting and polarization of well-known group-fre-

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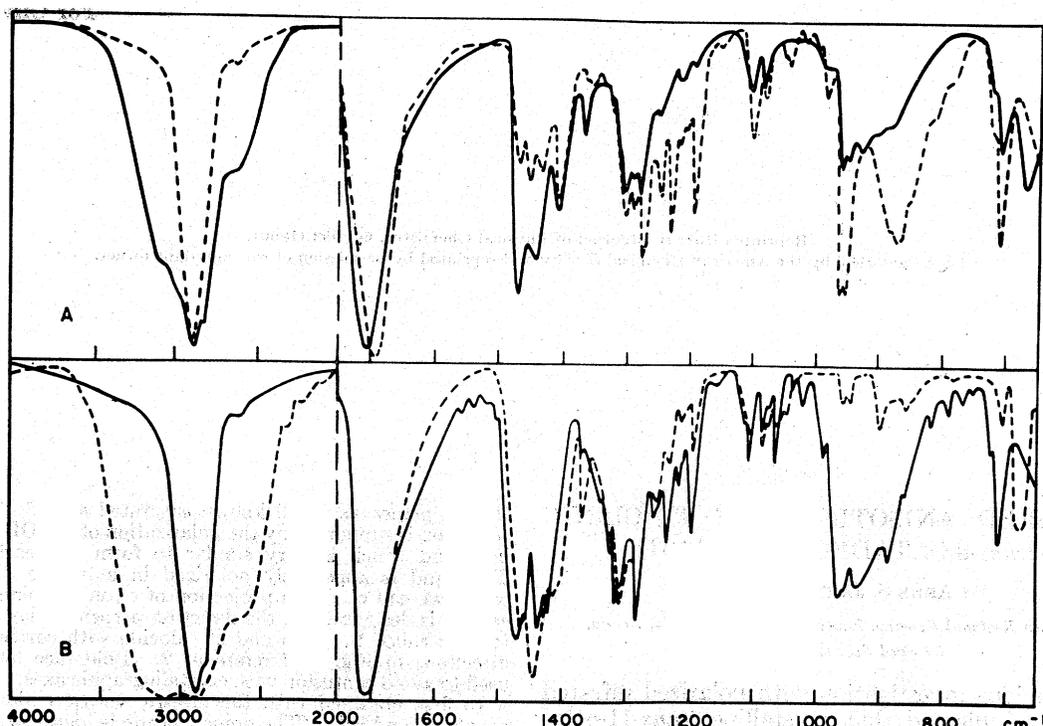


Fig. 1.—Infrared spectrum of *trans*-8-octadecenoic acid: A, electric vector along a (solid line) and b (dotted line); B, electric vector within the *ac'* plane, approximately perpendicular to *c'* (solid line) and parallel to *c'* (dotted line).

quency bands listed in Table I. Bands which are sufficiently free from extensive overlap have been chosen.

TABLE I  
POSITION AND POLARIZATION OF SOME GROUP-FREQUENCY BANDS

Description	Cm. <sup>-1</sup>	Polarization	
		ab plane	ac plane
(Carboxyl bands)			
OH str.	3100	a	to <i>c'</i>
C=O	1706	a	to <i>c'</i>
		b	
OH o.o.p. bend.	940	a	⊥ to <i>c'</i>
		b	⊥ to <i>c'</i>
COO def.	676	a	to <i>c'</i>
(CH <sub>2</sub> bands)			
CH <sub>2</sub> sym. str.	2850	a + 30°	⊥ to <i>c'</i>
CH <sub>2</sub> bend	1469	a + 30°	
CH <sub>2</sub> rock	719	b + 30°	⊥ to <i>c'</i>
( <i>trans</i> -HC=CH— bands)			
HC=CH o.o.p. bend.	966	a + 75°	⊥ to <i>c'</i>
		959	a + 75°

All OH bonds seem roughly parallel to each other and to the main axes of the molecules. The splitting of the C=O stretching and OH out of plane (o.o.p.) bending bands into oppositely polarized branches indicates two sets of carboxyl groups with non-parallel planes. The frequency difference between the 940 and 881  $\text{cm.}^{-1}$  branch of the OH bending band is much larger than is usually observed for factor group splitting and could mean that non-equivalent sites are occupied. The relative polarization of the CH<sub>2</sub> bands is correct and suggests that the major portions of the hydrocarbon chains are parallel to each other, but probably not parallel to the planes of any of the carboxyl groups. The —HC=CH— o.o.p. bending band is split into a doublet, both components being polarized the same way: perpendicular to the chains but neither perpendicular nor parallel to CH<sub>2</sub> or carboxyl bands.

The molecules, like the ones of the previously studied *trans*-11 acid,<sup>2</sup> seem to be considerably twisted, but the resulting structure must be different: roughly parallel hydrocarbon chains (strongly tilted with respect to the layers of end groups<sup>3</sup>) connected to non-parallel carboxyl groups in a triclinic over-all structure.