ACTA CHEMICA SCANDINAVICA 12 (1958) 777—792

Short Communications

The Crystal Structure of (—)-2-Methyl-2-Ethyleicosanoic Acid

ERIK von SYDOW

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

In connection with crystal structure investigations of normal and branched chain fatty acids [1-3], the molecular packing of (—) - 2 - methyl - 2 - ethyleicosanoic acid ($C_{23}H_{46}O_2$) has been determined. Only one X-ray investigation of a fatty acid substituted with a larger group than a methyl group is published: the unit cell dimensions of 14-DL-ethylhexadecanoic acid by Clark and Chu [4].

Ställberg-Stenhagen [5] points out that (—)-2-methyl-2-ethyleicosanoic acid crystallizes from light petroleum (b.p. 40—60°C) in a very beautiful way. The crystals are extremely long (5 cm) and lath-shaped, and they have a lustrous appearance. The racemic form of the acid does not crystallize so easily. No polymorphism is reported or observed.

The shape and the optical properties of the crystals indicated an orthorhombic space group, which was confirmed by the single crystal X-ray investigation, from which the following data was obtained:

$a = 8.150$, $b = 9.214$, $c = 31.50$ Å (± 0.2 %)
$d_{calc.} = 0.996$ gcm^{-3}, $d_{meas.} = 0.991$ gcm^{-3},
4 molecules per unit cell.

Absent reflexions: ($h00$) when h odd, ($0k0$) when k odd.
Space group: D_2^3—$P\,2_12_12$ (No. 18).

Sharpened Patterson projections along the three axes were calculated. From these and from the reciprocal lattice the subcell, *i. e.* the cell which describes the repetition in and of the hydrocarbon chains, was evaluated (Fig. 1). Its dimensions are $a_s = a = 8.150$, $b_s = b = 9.214$ and $c_s = 2.551$ Å (± 0.2 %), 8 CH_2-groups per subcell and space group D_2^3—$P\,2_12_12$ with $x_1 = 0.315$, $y_1 = 0.205$, $z_1 = 0$ and $x_2 = 0.315$, $y_2 = 0.295$, $z_2 = 0.500$. The chains are parallel and run parallel with c_s and c, and all the chain planes are also parallel with each other and with the $_sc_s$-plane (bc-plane). This subcell has never been found before.

Knowing the subcell structure and the main cell symmetry, the positional parameters of the atoms in the hydrocarbon chains could be directly determined. From spatial considerations the rest of the atoms were placed in the main cell and cycles of structure factor calculations and electron density projections along the shortest axes were performed. The molecular packing is shown schematically in Fig. 2. The structure will be refined in three dimensions.

There are two particularly interesting things in this structure: the new subcell and the hydrogen bond system. This subcell will be called O ∥ as compared with O ⊥ for the common orthorhombic chain pack-

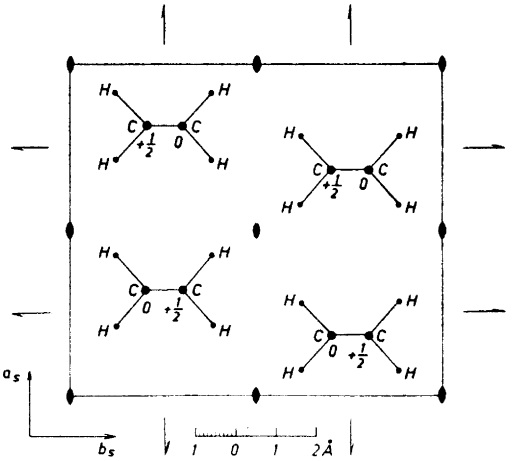

Fig. 1. The new orthorhombic subcell O ∥.

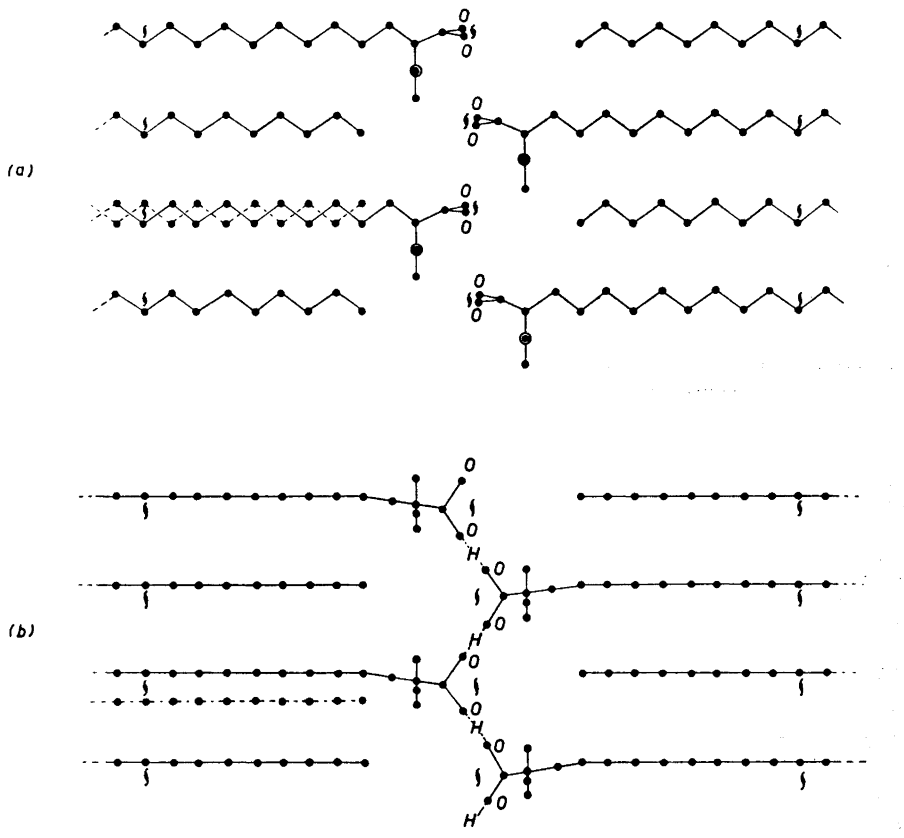

Fig. 2. (a) Schematic view along the *a*-axis and (b) along the *b*-axis of (—)-2-methyl-2-ethyleicosanoic acid.

ing [1], in which every second chain plane is approximately perpendicular to the others, and with T ∥ for the triclinic chain packing [1], in which all chain planes are parallel. Following a suggestion by Vand [6], the crystal structure of (—)-2-methyl-2-ethyleicosanoic acid should be classified as O ∥ (001), where (001) are the indices in the subcell of the *ab*-plane of the main cell.

A detailed comparison with the X-ray photographs given by Buerger [7] for *a*-sodium stearate hemihydrate reveals that that compound has the same hydrocarbon chain packing as (—)-2-methyl-2-ethyleicosanoic acid, *i. e.* O ∥.

The volume per CH_2-group in O ∥ is 23.95 Å^3, which is significantly larger than the corresponding volume in O | with comparable chain length [1] (23.3 Å^3). This means that the van der Waals interaction between chains of this length is larger in O ⊥ than in O ∥. In the case of (—)-2-methyl-2-ethyl-eicosanoic acid, however, this is compensated by the fact that, seen along the chains, the space occupied by two chains (Figs. 1 and 2) in O ∥ is the same as the space occupied by the branching groups and the carboxyl group of one molecule. The resulting hydrogen bond system (Fig. 2 b) is interesting in that one molecule is not bound to one other molecule (dimerization), as is usually the case with fatty acids [1-3], but to two other molecules, giving an one dimensional hydrogen bond helix parallel with the *a*-axis. Thus it is not surprising to find that

the *a*-direction is the same as the very much pronounced lath-direction of the crystals, mentioned above. The cleavage is also consistent with this arrangement. A somewhat similar hydrogen bond system has been found for formic acid [8], but never before for a long chain carboxylic acid.

Thanks are due to Professor S. Ställberg-Stenhagen for the crystals and to Professor E. Stenhagen for the measured density and his constant interest in this work. The expenses involved have been defrayed by grants from the *Swedish Natural Science Research Council.*

Full details of this work will be published later.

1. von Sydow, E. *Arkiv Kemi* **9** (1956) 231.
2. Abrahamsson, S. *Acta Cryst.* **9** (1956) 663
3. Abrahamsson, S. *Acta Cryst.* **11** (1958) *In press.*
4. Clark, G. L. and Chu, C.-C. *Acta Cryst.* **4** (1951) 470.
5. Ställberg-Stenhagen, S. *Arkiv Kemi* **3** (1951) 273.
6. Vand, V. *Acta Cryst.* **7** (1954) 697.
7. Buerger, M. J. *Amer. Mineral.* **30** (1945) 551.
8. Holtzberg, F., Post, B. and Fankuchen, I. *Acta Cryst.* **6** (1953) 127.

Received March 26, 1958.

The Fractionation of Spruce Wood

J. A. McPHERSON

Institutt for Treforedlingskjemi, Norges tekniske högskole, Trondheim, Norway

During the investigations on milled spruce wood, Björkman [1] was able to isolate material containing both lignin and carbohydrates and which was designated lignin-carbohydrate complexes (LCC).

It is proposed to report the preliminary results of further investigations on the extraction of wood with dimethyl sulphoxide (DMSO), of which brief mention has already been made [2].

The fractionation of milled spruce wood has been carried out by the successive extraction with dioxane, dimethyl formamide (DMF), DMSO and water, following which the cellulosic residues were recovered in yields of 41—43 %. These residues contained small amounts of lignin and hemicelluloses.

The extracts were fractionated at first by precipitation with selective solvents, but in an effort to avoid coprecipitation, later work involved distribution on columns of alumina, sand, or metallic oxides. However, when these were found to degrade the lignin, Celite columns were used instead. But in each case it was possible to isolate a series of lignin-carbohydrate complexes, together with relatively pure lignin and hemicellulose fractions. Except in one case where a small amount of a fraction containing glucose and mannose only (1:1.24) together with small amounts of lignin, was isolated from an alumina column, the LCC even where the lignin content was very small, still contained carbohydrates in the same approximate ratio as in the original hemicelluloses.

In one series of fractionations of milled spruce wood, the total amount extracted (31 %) was recovered almost entirely in the dioxane (9 %), DMF (7 %), DMSO (11.2 %) and the aqueous extracts (2 %). The difference is to be found in the DMSO mother liquors which were not further investigated in this series. The dioxane extract yielded a series of lignin fractions (CH_3O, 13—15 %) containing small amounts of carbohydrates, while the DMF extract gave a series of LCC (CH_3O, 5—12 % and lignin 10—90 %). Both the DMSO and the aqueous extracts could be largely precipitated by ethanol, yielding LCC material with 4 % CH_3O and about 22 % lignin. Whether the DMSO extract was precipitated by dioxane, ethanol or benzene, the complexes obtained still had methoxyl contents of about 3.5—4 % and lignin of about 22 %. Refractionations of these LCC gave a number of widely different fractions, with respect to their lignin content. Such fractionations were usually carried out on Celite columns with a combination of various solvent systems, *e. g.* ethyl acetate-acetic acid-water, butanol-pyridine-water or DMF-dinitromethane-water *etc.*

Intermediate lignin fractions, soluble in benzene and sometimes ether, were obtained in the first fractions from the Celite columns.

Since the relative proportion of the lignin to hemicellulose in the LCC modifies the solubility of the complex it was not surprising that LCC were isolated from clear solutions of benzene, dioxane, ethanol, water etc. Perhaps better methods for their isolation may be based on electrophoretic techniques.