On the Crystal Structure of 9DL-Methyloctadecanoic Acid

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9DL-Methyloctadecanoic acid, $C_{18}H_{37}COOH$, is triclinic with $a = 4.97$ Å, $b = 14.77$ Å, $c = 51.9$ Å, $\alpha = 165° 6'$, $\beta = 90°$, $\gamma = 90°$. The cell contains two molecules. The racemic acid has a centre of symmetry, confirming space group C_i^1-$P\bar{1}$. The hydrocarbon chains are arranged in a distorted triclinic packing. The angle of tilt is 18°, the acid being more tilted than any known fatty acid. The molecules must adopt such an angle to allow the branching methyl groups to accommodate themselves in the space between the ends of two carbon chains. The structure represents a rather rigid framework.

Introduction

Five years ago a programme of crystal-structure investigations of compounds with long hydrocarbon chains was taken up at this Institute, in connexion with the extensive chemical studies of such compounds by Prof. E. Stenhagen and his collaborators at the Institute of Medical Chemistry, University of Uppsala.

Thus, von Sydow has determined the structures of the different crystal forms of normal-chain carboxylic acids, the general features of which are given in a recent paper (von Sydow, 1956a).

As a natural extension, branched-chain fatty acids are being investigated. Such acids are of technical and biological importance and a knowledge of their crystal structures is, therefore, highly desirable.

A fundamental problem, in this connexion, is the effect of a branching methyl group in different positions in a long-chain carboxylic acid. The author has, therefore, started an investigation of the series of methyloctadecanoic acids, this paper representing the first contribution to this field. Structure determinations on other members of the series* are at present in progress.

So far, only one branched long-chain compound has been given a more detailed study by X-ray methods. The structure of isopalmitic acid has been derived by Stenhagen, Vand & Sim (1952). Clark & Chu (1951) have given single-crystal data for the iso and ante-iso acids of the series of methyloctadecanoic acids. As usual with long-chain compounds, several reports concerning the long spacings of some of these acids are found, e.g. Velick (1944, 1947), Ställberg-Stenhagen (1946, 1948, 1949) and Hallgren (1956).

Preparation of crystals

The pure 9DL-methyloctadecanoic acid was synthesized in Prof. E. Stenhagen's laboratory by Hallgren (1956).

* The complete series of racemic methyloctadecanoic acids has been kindly provided by Prof. James Cason of the University of California.

It had a melting point of 38·7–39·2° C. Though the acid has been prepared by several authors, no polymorphism has been observed (cf. Hallgren, 1956). The crystals obtained had no regular form and were rather hard in comparison with the soft flaky crystals of normal-chain acids. They were found to be biaxial positive and showed no twinning. Good crystals for the X-ray work were grown from the melt.

X-ray data

Rotation and zero- and n-layer Weissenberg photographs about the a and b axes were taken with Cu K radiation, using a calibrated camera. The following data were obtained, selecting the c axis parallel to the chain direction:

Molecular formula: $C_{19}H_{38}O_2$.
Molecular weight: 298·49.
Unit cell: triclinic.

$a = 4.97 \pm 0.02$, $b = 14.77 \pm 0.07$, $c = 51.9 \pm 0.3$ Å.
$\alpha = 165° 6' \pm 30'$, $\beta = 90° \pm 30'$, $\gamma = 90° \pm 30'$.

For the computations a unit cell with a different c axis was chosen and this cell will be used in the text (Fig. 2):

$a_1 = a = 4.97$, $b_1 = b = 14.77$, $c_1 = 15.07 \pm 0.09$ Å.
$\alpha_1 = 115° 30' \pm 30'$, $\beta_1 = \beta = 90°$, $\gamma_1 = \gamma = 90°$.

For both cells the following data are applicable:

Two molecules per unit cell.
Number of electrons: 336.
Density calculated: 0.991 ± 0.010 g.cm.$^{-3}$.
Density measured: 0·998 g.cm.$^{-3}$.
Space group: C_i^1-$P\bar{1}$.

The absence of the piezo-electric effect is consistent with a centre of symmetry.

$(0kl)$ reflexions up to $\theta = 52°$ were recorded. Two observers estimated the intensities by eye, using the multiple-film technique of de Lange, Robertson &

Woodward (1939). The normal Lorentz and polarization factors were applied during the calculation of observed structure factors. These were brought to an absolute scale by comparison with calculated structure factors in the later stages of the investigation. No absorption correction was made.

Patterson projection

A Patterson projection along the shortest axis was calculated, the Fourier summations being carried out on the Hägg–Laurent machine (1946). A sharpening was achieved by a modifying function suggested by Lipson & Cochran (1953, p. 172):

$$M(S) = \left(\frac{1}{\bar{f}}\right)^2 \exp\left(-\frac{\pi^2}{p} S^2\right) \text{ with } p = 7\cdot25 .$$

In the projection, three rows of peaks appeared, indicating that three carbon chains pass through the cell. From the direction of the rows, the chain axes were found to lie approximately parallel to the (013) planes. This is consistent with (013) being by far the strongest reflexion. The projection gave the carbon–carbon distances and showed that the planes of the carbon chains could not be far from parallel to the projection direction.

Subcell

In the reciprocal lattice the hydrocarbon chain should give rise to small groups of very strong reflexions forming a sublattice. Such groups were found, of course, but they were large and contained moderately strong reflexions, indicating distortions in the carbon chain. The dimensions of the subcell were calculated, however, to be approximately equal to those of the triclinic subcell reported by Vand & Bell (1951) and von Sydow (1956a) for the triclinic packing of hydrocarbon chains. It is, therefore, rather certain that the chains of the acid have this packing, even though irregularities are to be expected. The orientation of the subcell within the main cell is such that the c_s edge

of the subcell is parallel to the (013) planes, and the a_1 edge of the main cell is the short diagonal of the $a_s b_s$ face of the subcell.

Structure factors and electron-density projections

In the triclinic cell the true racemic acid has, necessarily, a centre of symmetry (confirming the space group C_i^1–$P\bar{1}$; Hägg, 1944). This fact, together with the information from the Patterson projection, led to the assumption of a molecular arrangement mainly as shown in Fig. 2.

As there seemed to be distortions in the carbon chain, no attempt was made to calculate coordinates from the carbon positions in the triclinic subcell determined by Vand & Bell (1951). For the first calculation of (0kl) structure factors, coordinates were instead taken from a trial structure with all the carbon atoms of the chain placed equally spaced along a straight line in accordance with the result of the Patterson projection. The two oxygen atoms and the branching methyl carbon atom were placed in the most probable way.

Atomic scattering curves were taken from McWeeny (1951), using for oxygen $f = \frac{1}{3}(f^\perp + 2f'')$ and for carbon the values for 'valence states'. Great simplifications are possible in the structure-factor calculations when assuming a periodic carbon chain. The subcell

Table 1. *Atomic coordinates*

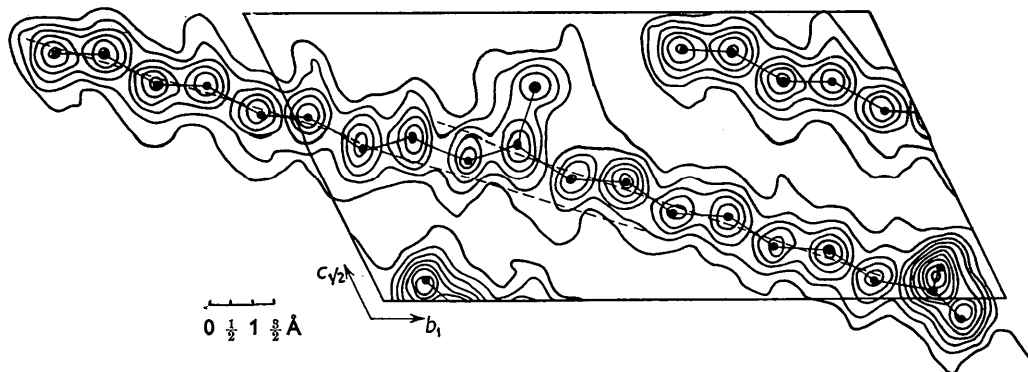| Atom	y/b_1	z/c_1	Atom	y/b_1	z/c_1
O_1	0·085	0·037	C_{10}	0·248	0·248
O_2	0·922	0·055	C_{11}	0·176	0·283
C_1	0·893	0·015	C_{12}	0·089	0·268
C_2	0·805	0·031	C_{13}	0·024	0·317
C_3	0·756	0·085	C_{14}	0·949	0·321
C_4	0·669	0·092	C_{15}	0·886	0·373
C_5	0·619	0·145	C_{16}	0·811	0·375
C_6	0·533	0·153	C_{17}	0·748	0·428
C_7	0·483	0·206	C_{18}	0·673	0·430
C_8	0·397	0·213	C_{19}	0·408	0·365
C_9	0·339	0·273			

Fig. 1. Electron-density projection along the shortest axis of 9DL-methyloctadecanoic acid. Contours are given at intervals of 1 e.Å^{-2}, starting with 1 e.Å^{-2}. The dashed lines represent the centre-lines of respective chain parts.

Table 2. *Observed and calculated structure factors*

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
000	—	336	036	12	−11	$06\bar{5}$	14	−12
001	29	29	037	5	5	$06\bar{6}$	4	4
002	11	−18	038	4	−4	$06\bar{7}$	7	7
003	51	50	039	9	8	$06\bar{8}$	<2	0
004	<1	4	$03\bar{1}$	<1	1	$06\bar{9}$	6	3
005	13	15	$03\bar{2}$	16	−17	$0,6,\overline{10}$	8	8
006	10	−10	$03\bar{3}$	4	7	$0,6,\overline{11}$	4	4
007	<1	1	$03\bar{4}$	10	−11	$0,6,\overline{12}$	<2	1
008	<2	−3	$03\bar{5}$	8	−8			
009	5	−7	$03\bar{6}$	<1	1	070	24	−22
0,0,10	3	−5	$03\bar{7}$	<1	2	071	10	−11
0,0,11	<2	0	$03\bar{8}$	12	−12	072	5	−6
			$03\bar{9}$	<2	3	073	<2	−3
010	19	20	$0,3,\overline{10}$	7	2	$07\bar{1}$	21	−21
011	10	7	$0,3,\overline{11}$	3	3	$07\bar{2}$	8	−7
012	35	34	$0,3,\overline{12}$	9	11	$07\bar{3}$	5	−6
013	152	152	$0,3,\overline{13}$	3	−2	$07\bar{4}$	6	−6
014	18	19				$07\bar{5}$	<2	−1
015	12	−16	040	16	−13	$07\bar{6}$	<2	−4
016	9	9	041	<1	−2	$07\bar{7}$	2	2
017	6	7	042	12	−15	$07\bar{8}$	7	2
018	5	−7	043	<1	−3	$07\bar{9}$	<2	0
019	5	−9	044	<1	−4	$0,7,\overline{10}$	5	2
0,1,10	<2	1	045	<2	1	$0,7,\overline{11}$	4	5
$01\bar{1}$	8	8	046	<2	−2	$0,7,\overline{12}$	<2	2
$01\bar{2}$	22	20	047	3	−1			
$01\bar{3}$	12	−13	048	12	−13	080	<2	−2
$01\bar{4}$	31	30	049	<2	−2	081	<2	−5
$01\bar{5}$	11	−7	$04\bar{1}$	15	−17	082	<2	−4
$01\bar{6}$	<2	−1	$04\bar{2}$	<1	−2	083	10	−12
$01\bar{7}$	6	−5	$04\bar{3}$	27	−28	$08\bar{1}$	4	3
$01\bar{8}$	5	−3	$04\bar{4}$	3	3	$08\bar{2}$	8	−6
$01\bar{9}$	2	−2	$04\bar{5}$	16	−16	$08\bar{3}$	<2	1
$0,1,\overline{10}$	4	−6	$04\bar{6}$	5	−4	$08\bar{4}$	<2	−2
$0,1,\overline{11}$	<2	−2	$04\bar{7}$	6	1	$08\bar{6}$	3	4
$0,1,\overline{12}$	<2	−1	$04\bar{8}$	6	4	$08\bar{7}$	2	1
$0,1,\overline{13}$	7	−8	$04\bar{9}$	20	19	$08\bar{8}$	<2	0
			$0,4,\overline{10}$	<2	2	$08\bar{9}$	7	6
020	4	−1	$0,4,\overline{11}$	<2	−1	$0,8,\overline{10}$	3	4
021	24	23	$0,4,\overline{12}$	4	7	$0,8,\overline{11}$	<2	0
022	44	−44	$0,4,\overline{13}$	3	4	$0,8,\overline{12}$	<2	2
023	5	10				$0,8,\overline{13}$	<2	2
024	15	5	050	11	−11	$0,8,\overline{14}$	8	7
025	<2	1	051	17	−18	$0,8,\overline{15}$	<2	2
026	44	44	052	8	−11			
027	7	−5	053	<1	1	092	4	4
028	5	−10	054	5	−5	093	4	4
029	4	2	057	<2	1	$09\bar{1}$	<2	0
0,2,10	<2	−2	058	<2	4	$09\bar{2}$	7	7
$02\bar{1}$	5	5	$05\bar{1}$	17	−17	$09\bar{4}$	6	4
$02\bar{2}$	7	8	$05\bar{2}$	19	−23	$09\bar{6}$	<2	1
$02\bar{3}$	4	2	$05\bar{3}$	<1	1	$09\bar{7}$	6	7
$02\bar{4}$	12	−10	$05\bar{4}$	29	−25	$0,9,\overline{10}$	3	9
$02\bar{5}$	10	10	$05\bar{5}$	<2	−7	$0,9,\overline{11}$	6	8
$02\bar{6}$	10	−5	$05\bar{6}$	31	29	$0,9,\overline{12}$	2	2
$02\bar{7}$	5	−6	$05\bar{7}$	8	−8	$0,9,\overline{13}$	5	0
$02\bar{8}$	<2	1	$05\bar{8}$	4	2	$0,9,\overline{14}$	4	−2
$02\bar{9}$	6	−5	$05\bar{9}$	12	5	$0,9,\overline{15}$	6	−5
$0,2,\overline{10}$	3	4	$0,5,\overline{10}$	6	6			
$0,2,\overline{11}$	10	−11	$0,5,\overline{11}$	5	3	0,10,5	6	6
$0,2,\overline{12}$	3	3	$0,5,\overline{12}$	<2	1	$0,10,\bar{2}$	4	4
$0,2,\overline{13}$	<2	4				$0,10,\bar{6}$	6	6
$0,2,\overline{14}$	<2	−2	060	18	−18	$0,10,\bar{7}$	<2	−1
$0,2,\overline{15}$	2	3	061	12	−15	$0,10,\bar{8}$	<2	10
			062	6	−7	$0,10,\bar{9}$	<2	1
030	2	1	063	6	−6	$0,10,\overline{10}$	4	1
031	21	−20	064	<2	−1	$0,10,\overline{11}$	9	−5
032	10	10	$06\bar{1}$	15	−12	$0,10,\overline{12}$	17	−15
033	11	−10	$06\bar{2}$	21	−22	$0,10,\overline{13}$	<2	−2
034	<1	1	$06\bar{3}$	21	−20	$0,10,\overline{14}$	<2	0
035	21	−23	$06\bar{4}$	16	−15	$0,10,\overline{15}$	3	−3

Table 2 (cont.)

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
0,11,$\bar{6}$	< 2	1	0,12,$\bar{1}$	< 2	2	0,12,$\overline{14}$	< 2	0
0,11,$\bar{7}$	12	9	0,12,$\bar{3}$	< 2	2			
0,11,$\bar{8}$	16	− 8	0,12,$\bar{4}$	13	10	0,13,$\bar{1}$	8	8
0,11,$\bar{9}$	31	−26	0,12,$\bar{6}$	29	−23	0,13,$\bar{3}$	14	−12
0,11,$\overline{10}$	< 2	− 1	0,12,$\bar{7}$	< 2	1	0,13,$\bar{4}$	6	4
0,11,$\overline{11}$	6	− 3	0,12,$\bar{8}$	< 2	1	0,13,$\bar{9}$	< 2	2
0,11,$\overline{12}$	5	− 5	0,12,$\bar{9}$	6	− 6	0,13,$\overline{10}$	4	− 4
0,11,$\overline{13}$	4	− 2	0,12,$\overline{10}$	2	− 2	0,13,$\overline{11}$	< 2	0
0,11,$\overline{14}$	2	− 2	0,12,$\overline{11}$	2	− 2			
0,11,$\overline{15}$	< 2	0	0,12,$\overline{12}$	2	− 2	0,14,$\bar{3}$	< 2	1
			0,12,$\overline{13}$	3	− 3	0,14,$\bar{4}$	6	4
0,12,0	5	7						
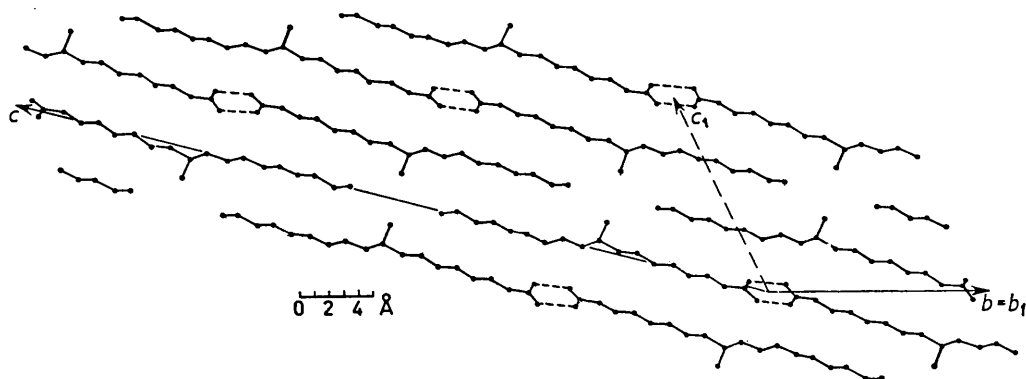
Fig. 2. The arrangement of the molecules of 9DL-methyloctadecanoic acid, as viewed along the shortest axis.

theory was, therefore, adopted as applied by Vand & Bell (1951).

Thus, the signs of 35 structure factors were established and an electron-density projection along the shortest axis was calculated. All the atoms were rather well resolved, except those of the carboxyl group and the branching methyl group. The projection showed clearly that the chain was appreciably bent. The atoms were given new coordinates, which were refined by the usual method of successive approximations. As distortions had been found in the carbon chain, the subcell concept was, of course, not applicable any longer, and all the atoms had to be treated separately in the calculations.

The final refinement of the atomic parameters was accomplished by several difference syntheses. Soon, the positive peaks on the difference map could be interpreted as hydrogen atoms which were included in the structure-factor calculations at this stage. The atoms were given approximate coordinates calculated from the data of Vainshtein & Pinsker (1950). The hydrogen contribution to the structure factors was small, except for a few reflexions.

To obtain better agreement between observed and calculated structure factors, a temperature factor was applied: exp $(-B \sin^2 \theta/\lambda^2)$ with $B = 6\cdot2$ Å^2. The final electron-density projection is shown in Fig. 1. The coordinates of the heavier atoms are listed in Table 1, and observed and calculated structure factors in

Table 2. The reliability index, R_1, is 0·14, non-observed reflexions being omitted.

Accuracy of coordinates

In order to estimate the accuracy of the atomic coordinates in the projection, the standard deviations were calculated using the formulae of Cruickshank (1949a, 1949b, 1954). The rather large number of parameters in comparison with independent reflexions was taken into account. Following a suggestion by Dr I. Lindqvist, the central curvature at each atomic centre,

$$\left(\frac{\partial^2 \varrho}{\partial y^2}\right)_n = \left[-\frac{4\pi^2}{b^2 A}\left\{\Sigma k^2 F \cos 2\pi\left(\frac{ky}{b}+\frac{lz}{c}\right)\right\}\right]_n,$$

was obtained from a modified F synthesis where the F-values had been multiplied by k^2. This synthesis gave a clear picture of the relative accuracy of the coordinates. It was thus found that all the atoms had approximately the same standard deviation. The branching carbon atom was an exception, however, its deviation being $\sigma(y) = \sigma(z) = 0\cdot03$ Å, as compared with the average value for the other atoms of $\sigma(y) = 0\cdot02$ Å. These values certainly represent the maximum deviations, but, as no fine details of the structure can be determined from one projection only, they will suffice for the discussion below. Thus, any difference in bond lengths between atoms in the chain less than 0·07 Å will be regarded as insignificant.

Discussion of the results

All the chain planes are parallel, confirming the earlier statement of a triclinic chain packing.

The first part of the chain is quite regular, except for the carbon atom (C_1) of the carboxyl group. In the projection, the C_1–C_2 distance is, thus, 0·15 Å longer than the average distance between the other atoms (C_2–C_8). Here, the chain axis seems to run parallel to the b_1c_1 face, so that the distance between alternate carbon atoms in the chain can be obtained from the projection. The average value found is 2·55 Å. In the region of the atoms C_9–C_{12}, the chain is strongly bent, the resultant effect being a displacement of the centre-line of the atoms C_{13}–C_{18} from that of the first chain part. The separation of the centre-lines in the vicinity of the atom C_9 is 0·85 Å.

From the distances in the projection, it can be concluded that the chain must be bent in the a_1 direction, too, and that the bending is probably accompanied by a twist of the chain plane. In the end of the chain, every second carbon–carbon distance is 0·30 Å longer than the others, meaning, of course, that the chain axis is no longer parallel to the b_1c_1 plane.

The most striking feature in Fig. 2, where several molecules are shown, is the enormous tilt of the chain axes to the (001) planes. The angle of tilt for the regular part (C_2–C_8) is 18°, calculated from the average difference of z coordinates between alternate carbon atoms. The molecules are, thus, more tilted than those of any known fatty acid. This is easily understood from Fig. 2. The long hydrocarbon chains tend to arrange in one of the two packings suitable for fatty acid carbon chains (cf. von Sydow, 1956a), in this case the triclinic. The large volume of the branching methyl group cannot possibly be accommodated into the packing when the neighbouring chain passes the branch. The molecules must, therefore, find such an angle that the methyl groups can expand into the space between the ends of two chains. The tilt of iso-palmitic acid, 43–45° (Stenhagen et al., 1952), which angle, too, is smaller than those of normal-chain acids (approximately 60°, von Sydow, 1956a), is also due to this effect.

With this tilted arrangement, however, the carboxyl groups have been forced into the chain packing. They do not fit well, the observed irregularities in the chain being the consequence. Owing to the pressure of the oxygen atoms, the carbon chains must separate a little. This deformation is just possible without disturbing the whole packing, as the chains can bend into the gaps between the chain ends. The distortions are severe, however, and the end of the carbon chain is not allowed to become quite parallel to the first regular part.

The molecules are, as with other fatty acids, linked together in dimers by hydrogen bonds between the carboxyl groups, alternate layers of carboxyl groups

and methyl groups being formed. In normal fatty acids with a more vertical arrangement of the chains, the methyl group layers have rather weak van der Waals binding forces, causing the crystals to grow in thin plates. These crystals are easily split up in the (001) planes and twinning on these planes is common (cf. von Sydow, 1956a). This acid has no such layers of weak van der Waals interaction, as can be seen from Fig. 2. The forces between two chains are very strong, and, as the chains are almost parallel to the (001) planes, these forces have large components perpendicular to these planes. The methyl-group layers are, therefore, held firmly together and the forces in the carboxyl-group layers are also strengthened. The branching methyl groups probably increase the interaction between the chain ends. Generally, it can be stated that this tilted structure represent a rather rigid framework consistent with the physical properties of the crystals from the acid. These all grow in hard irregular blocks and show neither cleavage nor twinning. A somewhat similar case has been observed by von Sydow (1956b) in the superstructure of form A of lauric acid, where no layers of weak interaction are found, either.

References

CLARK, G. J. & CHU, C.-C. (1951). Acta Cryst. 4, 470.

CRUICKSHANK, D. W. J. (1949a). Acta Cryst. 2, 65.

CRUICKSHANK, D. W. J. (1949b). Acta Cryst. 2, 154.

CRUICKSHANK, D. W. J. (1954). Acta Cryst. 7, 519.

HÄGG, G. (1944). The Svedberg 1884 30/8 1944, p. 140. Uppsala: Almqvist and Wiksell.

HÄGG, G. & LAURENT, T. (1946). J. Sci. Instrum. 23, 155.

HALLGREN, B. (1956). Ark. Kemi, 9, 389.

LANGE, J. J. DE, ROBERTSON, J. M. & WOODWARD, I. (1939). Proc. Roy. Soc. A, 171, 398.

LIPSON, H. & COCHRAN, W. (1953). The Determination of Crystal Structures. London: Bell.

McWEENY, R. (1951). Acta Cryst. 4, 513.

STÄLLBERG-STENHAGEN, S. (1946). Ark. Kemi Min. Geol. 22 A, No. 19.

STÄLLBERG-STENHAGEN, S. (1948). Ark. Kemi Min. Geol. 26 A, No. 12.

STÄLLBERG-STENHAGEN, S. (1949). Ark. Kemi, 1, 187.

STENHAGEN, E., VAND, V. & SIM, A. (1952). Acta Cryst. 5, 695.

SYDOW, E. VON (1956a). Ark. Kemi, 9, 231.