

The Crystal Structure of Tetradecanamide

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Tetradecanamide, $\text{NH}_2\text{CO}(\text{CH}_2)_{12}\text{CH}_3$, crystallizes in the monoclinic system with $a_0 = 9.83 \pm 0.03$, $b_0 = 5.61 \pm 0.03$, $c_0 = 27.98 \pm 0.03$ Å, $\beta = 95.1^\circ \pm 0.5^\circ$, and space group $P2_1/a$. The unit cell contains 4 molecules. The structure has been determined by means of two-dimensional projections. The molecules were found to occur in the crystal as dimers, packed into rows extending in the b direction, with the paraffin chains inclined to $46^\circ 40'$ from the b axis. The paraffin chains of adjacent rows are oppositely inclined, forming a crossed-chain structure.

Introduction

The study of the crystallography of the n -aliphatic amides (Turner & Lingafelter, 1955) has shown that all the members of the homologous series have essentially the same structure, although there appear to be certain minor variations. This paper presents the results of the determination of the structure of one member of the series, tetradecanamide, which was selected for this study both because suitable crystals were available from the work on the homologous series, and because the longer paraffin chain would be an aid in obtaining a first approximation to the structure despite the greater number of parameters. The structures of other members of the series are at present being investigated and will be reported later.

Experimental

The tetradecanamide crystals used in this study were obtained from an aqueous solution in the form of thin tablets on {001}, elongated in the b direction. The crystals used to obtain the intensity data were trimmed to square prisms with the a or b axis as prism axis.

From rotation and equi-inclination Weissenberg photographs, using $\text{Cu } K\alpha$ radiation, the unit-cell dimensions were found to be:

$$a_0 = 9.83 \pm 0.03, \quad b_0 = 5.61 \pm 0.03, \quad c_0 = 27.98 \pm 0.03 \text{ Å}, \\ \beta = 95.1 \pm 0.5^\circ.$$

Systematic absence of $(h0l)$ reflections for h odd and $(0k0)$ reflections for k odd indicated the space group to be $P2_1/a-C_{2h}^5$. There are four molecules per unit cell, the calculated density being 0.983 g.cm.^{-3} , as compared with the experimentally determined density of 0.984 g.cm.^{-3} .

The intensity data were obtained from photographs of the $(h0l)$ and $(0kl)$ nets taken with a Supper Weissenberg camera and with a Nonius integrating Weissenberg camera, integrating in one direction only,

using both multiple films and a range of exposure times. Both nickel-filtered and unfiltered Cu radiation were used.

The intensities were measured from the integrating Weissenberg photographs by means of a Moll-type microphotometer feeding into a Speedomax recorder, each reflection on a film being scanned normal to the direction of camera integration. The resulting curve for each reflection was then manually integrated and this value was taken as proportional to the integrated intensity. The correlation between X-ray intensities and microphotometer readings was established by the measurement of a series of timed-exposure spots. Very weak reflections were measured by the same procedure from ordinary Weissenberg photographs. Lorentz and polarization factors were applied, but no corrections were made for absorption. The resulting set of relative structure factors was placed on an absolute scale by comparison with calculated structure factors during the later stages of the structure determination.

Of the 35 $(00l)$ and 323 non-extinct $(h0l)$ reflections with $h \neq 0$ in the region covered by the photographs, 27 $(00l)$ and 219 $(h0l)$ reflections could be observed and measured. Of the possible 177 $(0kl)$ reflections with $k \neq 0$, 71 could be observed and measured.

Structure factors were computed from the atomic coordinates using Hartree scattering factors. CH_2 , CH_3 and NH_2 groups were treated as single atoms, adding $\frac{1}{2}(f_{0-2} - f_0)$ for each hydrogen atom to the scattering factor for the carbon or nitrogen atoms. The errors in the calculated structure factors introduced by this treatment of the hydrogen atoms proved to be small in all cases, except the (401) , (402) and (403) reflections, whose spacings and directions are such that the hydrogen atoms in their correct positions would have a maximum effect on the structure factors.

In order to attain agreement between observed and calculated structure factors it was necessary to apply an anisotropic temperature factor to the calculated structure factors.

Visual inspection of the Weissenberg photographs indicated that the maximum value of the temperature

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factor should be for the $(00l)$ reflections. It was then found that plots of

$$\log (F_c/F_o)/(\sin \theta/\lambda)^2 \text{ versus } \sin^2 \varphi$$

(where φ is the angle between a given plane and the (001) plane) gave fairly satisfactory lines both for the $(h0l)$ reflections and for the $(0kl)$ reflections. The temperature factors were therefore taken to be of the form $(A - C \sin^2 \varphi)$, with the values of the constants determined from these plots to be

$$\begin{aligned} A &= 6.9 \times 10^{-16} \text{ cm.}^2, \\ C &= 4.3 \times 10^{-16} \text{ cm.}^2 \text{ for } (h0l) \text{ reflections,} \\ C &= 2.3 \times 10^{-16} \text{ cm.}^2 \text{ for } (0kl) \text{ reflections.} \end{aligned}$$

The Fourier syntheses were computed with the aid of Patterson-Tunell and Beavers-Lipson strips, the final projections being evaluated at intervals of 3° along the a and c axes and 6° along the b axis.

Structure determination

Since there are four equivalent positions in the space group $P2_1/a$, the asymmetric unit consists of one molecule. In forming a trial structure the molecule was assumed to be planar and the paraffin chain to be straight, with C-C distances of 1.54 \AA and alternate carbon distances of 2.54 \AA . The amide group dimensions were assumed to be similar to those of acetamide (Senti & Harker, 1940).

The tilt of the paraffin chain from the c^* direction, as determined from the variation of d_{001} with chain length for the n -aliphatic amide series by Turner & Lingafelter (1955), is $46^\circ 20'$. The diffraction patterns of the n -aliphatic amides show a characteristic very intense reflection in the $(01l)$ row in a direction about 45° from the c^* direction, and three very intense adjacent reflections in the $(20l)$ row, the center reflection of the three having a direction of about 103° from the c^* direction in all cases. If these reflections are taken to indicate the orientation of the paraffin chain, then the chain must have components of tilt of about 13° toward the a axis and 45° toward the b axis.

An approximate set of z coordinates was obtained by first determining the z coordinates of propanamide by trial and error, where only a few parameters and reflections are involved. The positions of the amide group and the terminal methyl group were then applied to hexanamide, and the z coordinates of hexanamide were readily determined from the $(00l)$ intensities, yielding the distribution of carbon atoms along the paraffin chain. These coordinates were then applied to tetradecanamide, and a good agreement between observed and calculated structure factors was obtained.

The orientation of the plane of the paraffin chain was then readily derived from the components of tilt along the a and b axes and the distribution of the

carbon atoms in the c^* direction. It was found that this plane must be nearly parallel to the a axis.

The position of the molecule in the direction of the a axis was found by examination of the three intense reflections (200) , (201) and (202) . If the phase of one of these terms is taken arbitrarily there are two combinations of phases for the set which yield Fourier syntheses compatible with the z coordinates and the 13° tilt, but differing by a shift along the a axis. A trial structure was fitted to each case, and F_{203} , which was observed to have zero intensity, as well as F_{200} , F_{201} and F_{202} were calculated. F_{203} was found to be near zero in only one case. A more extensive set of structure factors for this case was found to agree well with the observed structure factors and this structure was refined by a series of Fourier syntheses. Since the phase of one reflection was chosen arbitrarily it was necessary to determine the true origin of the cell by calculation of several (hkl) structure factors from the final x , y and z coordinates for the two possible origins.

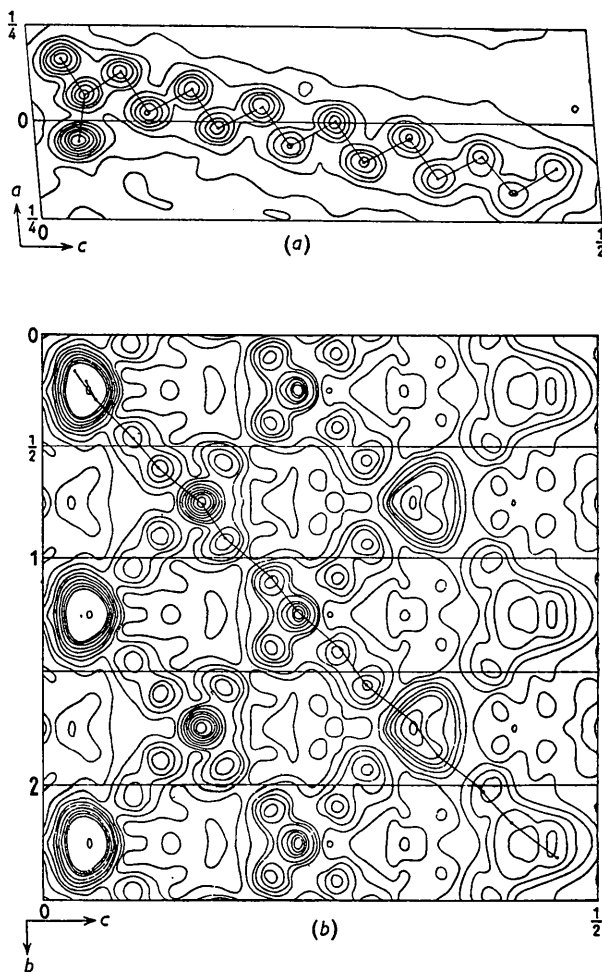


Fig. 1. (a) The $(h0l)$ electron-density projection of tetradecanamide. Contours are drawn at $1 \text{ e.}\text{\AA}^{-2}$ intervals.

(b) The $(0kl)$ electron-density projection of tetradecanamide. Contours are drawn at $1 \text{ e.}\text{\AA}^{-2}$ intervals, except in the polar-group peak, where the upper contours are omitted.

Table 1. *Observed and calculated structure factors*

hk l	F _{obs.}	F _{calc.}	hk l	F _{obs.}	F _{calc.}	hk l	F _{obs.}	F _{calc.}	hk l	F _{obs.}	F _{calc.}	hk l	F _{obs.}	F _{calc.}	hk l	F _{obs.}	F _{calc.}
00 0	---	+512	20 2	67	+ 75	4024	5	- 4	6024	4	- 1	80 4	8	- 7	10017	2	+ 4
00 1	45	+ 56	20 3	0	- 2	4025	5	- 2	60 1	5	+ 3	80 5	5	- 7	120 7	16	+ 19
00 2	0	+ 5	20 4	34	+ 40	4026	2	- 2	60 2	7	- 8	80 6	4	- 1	01 0	--	--
00 3	32	+ 36	20 5	9	- 10	40 1	9	+ 9	60 3	10	- 2	80 7	4	- 8	01 1	2	- 5
00 4	8	- 7	20 6	17	+ 18	40 2	20	- 17	60 4	10	- 13	80 8	4	+ 2	01 2	13	- 12
00 5	20	+ 17	20 7	14	- 12	40 3	11	- 8	60 5	12	- 5	80 9	16	- 15	01 3	16	- 20
00 6	17	- 15	20 8	3	+ 3	40 4	24	- 19	60 6	8	- 13	8010	13	- 9	01 4	13	+ 10
00 7	0	- 1	20 9	15	- 13	40 5	15	- 18	60 7	8	- 3	8011	42	+ 57	01 5	126	-152
00 8	22	- 22	2010	2	- 7	40 6	22	- 18	60 8	7	- 14	8012	24	+ 16	01 6	63	- 65
00 9	15	- 14	2011	12	- 12	40 7	12	- 21	60 9	4	+ 5	8013	11	+ 12	01 7	27	- 32
0010	30	- 28	2012	6	- 8	40 8	17	- 13	6010	9	- 18	8014	9	+ 8	01 8	28	- 29
0011	23	- 19	2013	7	- 4	40 9	11	- 19	6011	39	+ 36	8015	5	+ 3	01 9	14	- 16
0012	25	- 23	2014	12	+ 12	4010	9	- 6	6012	22	+ 32	8016	3	+ 4	0110	27	- 23
0013	24	- 21	2015	5	+ 2	4011	11	- 18	6013	24	- 33	8017	0	- 1	0111	38	- 28
0014	12	- 11	2016	4	0	4012	12	+ 21	6014	12	- 7	8018	0	+ 3	0112	0	- 3
0015	14	- 11	2017	5	+ 4	4013	37	- 35	6015	8	- 11	8019	0	- 2	0113	4	+ 2
0016	42	- 43	2018	5	+ 2	4014	29	- 28	6016	6	- 3	8020	0	+ 1	0114	8	+ 5
0017	11	- 10	2019	6	+ 6	4015	0	+ 3	6017	3	- 4	8021	3	- 3	0115	10	+ 8
0018	4	- 4	2020	4	+ 3	4016	0	+ 2	6018	3	0	8022	3	- 2	0116	9	+ 8
0019	0	0	2021	6	+ 5	4017	7	+ 8	6019	0	+ 1	8023	3	- 3	0117	11	+ 8
0020	4	+ 3	2022	4	+ 1	4018	7	+ 8	6020	0	+ 1	8024	3	- 2	0118	9	+ 9
0021	3	+ 3	2023	5	+ 5	4019	8	+ 10	6021	0	+ 2	8025	0	- 1	0119	8	+ 7
0022	5	+ 4	2024	0	0	4020	9	+ 9	6022	0	+ 1	8026	2	0	0120	7	0
0023	2	+ 3	2025	4	+ 4	4021	8	+ 7	6023	0	+ 1	8027	4	- 6	0121	13	+ 16
0024	5	+ 5	2026	0	0	4022	8	+ 7	6024	0	+ 1	8028	3	- 3	0122	7	+ 6
0025	3	+ 2	2027	0	+ 3	4023	6	+ 4	6025	0	0	100 0	10	- 4	0123	0	+ 5
0026	3	+ 5	2028	3	- 2	4024	7	+ 4	6026	2	+ 5	100 1	9	- 11	0124	0	- 1
0027	0	0	2029	0	- 1	4025	3	+ 3	6027	7	- 7	100 2	9	- 4	0125	0	+ 4
0028	3	+ 4	2030	11	+ 10	4026	4	+ 2	6028	4	- 7	100 3	9	- 10	0126	0	- 2
0029	0	- 2	2031	5	- 3	4027	2	+ 2	6029	4	+ 5	100 4	7	+ 1	0127	10	- 6
0030	5	+ 4	2032	7	- 4	4028	7	- 10	6030	3	+ 1	100 5	13	- 15	02 0	28	- 30
0031	0	+ 1	2033	5	- 3	4029	10	+ 7	6031	3	+ 3	100 6	0	- 2	02 1	17	- 20
0032	7	- 4	2034	3	- 2	4030	9	+ 7	80 0	8	- 5	100 7	24	+ 35	02 2	25	- 31
20 0	138	+151	40 0	15	- 17	60 0	0	+ 2	80 1	8	- 7	100 8	15	+ 7	02 3	14	- 14
20 1	93	+ 88	40 1	6	+ 25	60 1	2	+ 3	80 2	9	- 7	100 9	4	+ 7	02 4	18	- 25
20 2	165	-173	40 2	25	- 48	60 2	9	+ 9	80 3	5	- 2	10010	5	+ 3	02 5	15	- 14
20 3	27	- 20	40 3	11	- 22	60 3	15	+ 12	80 4	12	- 4	10011	2	+ 3	02 6	24	- 25
20 4	26	- 26	40 4	22	+ 31	60 4	7	+ 11	80 5	24	- 32	10012	2	+ 2	02 7	16	+ 4
20 5	11	- 8	40 5	16	+ 20	60 5	3	+ 7	80 6	3	+ 8	10013	2	+ 3	02 8	0	+ 5
20 6	7	- 7	40 6	16	+ 23	60 6	14	+ 16	80 7	12	+ 11	100 1	10	- 10	02 9	10	- 16
20 7	8	- 10	40 7	17	+ 21	60 7	13	+ 10	80 8	6	+ 6	100 2	9	- 6	0210	39	+ 45
20 8	8	- 10	40 8	16	+ 13	60 8	14	+ 12	80 9	8	+ 7	100 3	8	- 8	0211	31	+ 36
20 9	9	- 10	40 9	14	+ 17	60 9	13	+ 7	8010	8	+ 5	100 4	6	- 8	0212	17	+ 16
2010	11	- 15	4010	12	+ 11	6010	12	+ 11	8011	5	+ 5	100 5	4	- 3	0213	12	+ 13
2011	10	- 10	4011	10	+ 9	6011	10	0	8012	5	+ 2	100 6	4	- 4	0214	10	+ 10
2012	11	- 17	4012	8	+ 3	6012	7	+ 8	8013	3	+ 5	100 7	0	- 2	0215	5	+ 7
2013	9	- 9	4013	7	0	6013	5	- 4	8014	0	- 1	100 8	10	- 2	0216	0	+ 6
2014	14	- 17	4014	0	+ 2	6014	3	+ 4	8015	0	+ 4	100 9	16	- 30	0217	9	+ 2
2015	0	+ 2	4015	0	+ 4	6015	0	- 4	8016	0	- 4	10010	0	+ 2	0218	0	+ 2
2016	37	- 34	4016	0	+ 4	6016	0	0	8017	0	+ 2	10011	11	+ 14	0219	0	- 2
2017	27	- 20	4017	21	- 21	6017	4	- 5	8018	2	- 4	10012	11	+ 6	0220	0	+ 4
2018	31	+ 30	4018	30	+ 26	6018	0	- 4	8019	0	+ 1	10013	9	+ 13	0221	15	- 9
2019	17	+ 7	4019	26	+ 18	6019	11	+ 14	8020	3	- 2	10014	8	+ 4	0222	16	- 9
2020	12	+ 11	4020	14	- 10	6020	17	- 16	8021	8	- 9	10015	7	+ 10	03 0	--	--
2021	6	+ 3	4021	11	- 4	6021	21	- 14	80 1	9	- 6	10016	6	+ 3	03 1	0	+ 3
2022	3	+ 4	4022	10	- 9	6022	11	- 7	80 2	8	- 7	10017	4	+ 7	03 2	8	+ 12
20 1	14	+ 10	4023	10	- 4	6023	7	- 5	80 3	7	- 7	10018	4	+ 2	03 3	11	+ 11

The final electron-density map of the (*h*0*l*) projection is shown in Fig. 1(*a*).

The *y* coordinates were determined by means of the (0*kl*) projection. A trial structure was formed, using

the previous assumptions and the *x* and *z* coordinates. The *y* coordinates were expressed in the form *y*_{*i*} = *s*, where *s* is a constant. The best value of *s* was determined by computing the structure factors for the very

strong (015) reflection and for the weak (014) reflection for several values of s . An attempt was then made to refine y coordinates by means of Fourier syntheses. However, owing to the large angle of tilt of the paraffin chain and the mirror plane in this projection the chains were found to cross, so that several of the atomic peaks could not be resolved by this method. The y coordinates were refined instead by a series of difference syntheses, using only those terms in which $k = 1$ and $k = 2$ in the first few, then continuing with all available terms.

The electron-density map of the (0 kl) projection, computed from the final set of phases for the (0 kl) reflections is shown in Fig. 1(b).

The comparison of observed and calculated structure factors for the final structure is given in Table 1. The reliability coefficient $R = \sum |F_o| - |F_c| \div \sum |F_o|$ including all observed, non-zero reflections is 0.245. For the ($h0l$) projection $R = 0.251$, and for the (0 kl) projection $R = 0.201$. For the (00 l) reflections alone, $R = 0.126$.

The ($h0l$) electron-density projection shows a regular decrease in height of the carbon atom peaks with increasing distance from the polar group. This may be interpreted as an increase in thermal vibration of the atoms of the paraffin chain with increasing distance from the more strongly bound polar group. The application of individual temperature factors to allow for this effect would probably considerably increase the agreement between observed and calculated structure factors.

The atomic coordinates are given in Table 2. The y coordinates of atoms lying near the mirror plane

Table 2. The atomic coordinates of tetradecanamide

Atom	x/a	y/b	z/c
N	0.161	0.165	0.029
O	-0.048	0.212	0.039
C ₁	0.669	0.286	0.047
C ₂	0.128	0.466	0.082
C ₃	0.027	0.596	0.103
C ₄	0.086	0.764	0.143
C ₅	-0.014	0.916	0.163
C ₆	0.043	1.085	0.205
C ₇	-0.058	1.233	0.227
C ₈	0.004	1.404	0.269
C ₉	-0.100	1.557	0.291
C ₁₀	-0.035	1.724	0.333
C ₁₁	-0.139	1.877	0.356
C ₁₂	-0.083	2.012	0.396
C ₁₃	-0.178	2.156	0.421
C ₁₄	-0.112	2.318	0.462

in the (0 kl) projection are necessarily ambiguous. However, those coordinates were chosen which gave the most 'satisfactory' structure for the molecule. In the case of the atoms of the paraffin chain the choice of the alternate position would have shown just those atoms with ambiguous y coordinates deviating sharply from the plane of the paraffin chain. Again, the choice was made in the polar group to give the most satisfactory arrangement, but the alternate choice would

not make any great difference in the bond distances or the interaction of the polar group with other molecules.

Discussion

The interatomic distances and bond angles calculated from the atomic coordinates are shown in Table 3.

Table 3. Interatomic distances and angles of the tetradecanamide structure

Bond distances (Å)		Bond angles (°)		Alternate carbon distances (Å)	
N-C ₁	1.26	N-C ₁ -O	116.3	C ₁ -C ₃	2.41
O-C ₁	1.23	N-C ₁ -C ₂	113.1	C ₂ -C ₄	2.45
C ₁ -C ₂	1.49	O-C ₁ -C ₂	130.4	C ₃ -C ₅	2.52
C ₂ -C ₃	1.52	C ₁ -C ₂ -C ₃	112.9	C ₄ -C ₆	2.56
C ₃ -C ₄	1.46	C ₂ -C ₃ -C ₄	113.4	C ₅ -C ₇	2.58
C ₄ -C ₅	1.56	C ₃ -C ₄ -C ₅	115.4	C ₆ -C ₈	2.62
C ₅ -C ₆	1.48	C ₄ -C ₅ -C ₆	116.2	C ₇ -C ₉	2.60
C ₆ -C ₇	1.59	C ₅ -C ₆ -C ₇	116.2	C ₈ -C ₁₀	2.60
C ₇ -C ₈	1.51	C ₆ -C ₇ -C ₈	114.7	C ₉ -C ₁₁	2.47
C ₈ -C ₉	1.59	C ₇ -C ₈ -C ₉	114.8	C ₁₀ -C ₁₂	2.47
C ₉ -C ₁₀	1.51	C ₈ -C ₉ -C ₁₀	113.8	C ₁₁ -C ₁₃	2.55
C ₁₀ -C ₁₁	1.43	C ₉ -C ₁₀ -C ₁₁	113.9	C ₁₂ -C ₁₄	2.53
C ₁₁ -C ₁₂	1.44	C ₁₀ -C ₁₁ -C ₁₂	114.0		
C ₁₂ -C ₁₃	1.55	C ₁₁ -C ₁₂ -C ₁₃	117.4		
C ₁₃ -C ₁₄	1.55	C ₁₂ -C ₁₃ -C ₁₄	116.2		
Average	1.505	Average C-C-C	114.9	Average	2.534
Hydrogen bonds, N-H...O: intradimer 2.99 Å; interdimer 2.93 Å.					

The average C-C bond distance and its average deviation is 1.505 ± 0.048 Å. The average alternate carbon distance is 2.534 ± 0.059 Å. The average C-C-C angle is $114^\circ 55' \pm 53'$.

Polar group

The amide groups of two molecules are coupled by two N-H...O bonds of length 2.99 Å to form a dimer. The two tetradecanamide molecules forming a dimer are related by a center of symmetry, which,

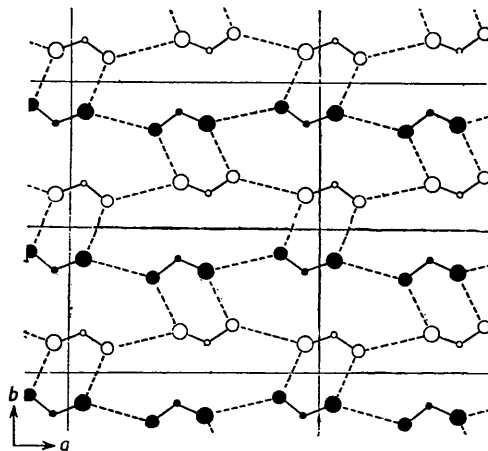


Fig. 2. A schematic projection on (001) showing the hydrogen-bond network between the polar groups of tetradecanamide. The paraffin chains are omitted for clarity.

for convenience, will be termed the center of the dimer. The N, O, C₁ and C₂ atoms of the two molecules forming a dimer are coplanar to within an average deviation of ± 0.035 Å. These polar groups are twisted from the planes of their paraffin chains so that, although the axes and planes of the paraffin chains are parallel, they are neither colinear nor coplanar. Each molecule of a dimer is also coupled by a N-H...O bond of length 2.93 Å to its nearest neighbor in the *a* direction.

This results in the two-dimensional system of hydrogen bonds illustrated in Fig. 2. Atoms falling below the plane of the network, whose paraffin chains would extend downward, are shown as solid circles; and those above the plane of the network, whose paraffin chains would extend upward, are shown as open circles. This structure is quite similar to the structure proposed by Copley, Zellhoefer & Marvel (1938) for amides on the basis of the solvent behavior of methanamide and ethanamide, in which dimers are coupled by hydrogen bonds into indefinite polymers.

The paraffin chain

The plane of the carbon atoms (C₂-C₁₄) of the paraffin chain of tetradecanamide may be described, relative to the *a*, *b* and *c** axes, by the equation:

$$0.346x + 1.018y - 0.894z = 1.$$

The average deviation of the carbon atoms from this plane is ± 0.044 Å. The chain may therefore be considered planar within the accuracy of the coordinates. Further, there is no significant curvature of the chain. Any possible distortions of the paraffin chain, such as curvature or twist, are of smaller magnitude than the accuracy of the coordinates and could only be demonstrated by a considerably more accurate determination of the structure.

Intermolecular structure

The mode of packing of tetradecanamide is most conveniently considered in terms of the dimers rather than the single molecules. The dimers are arranged, parallel to each other, in rows extending in the *b* direction (see Fig. 3(a)), each dimer being related to the preceding one by a fixed translation, the *b* translation of 5.61 Å. The axes of the paraffin chains are inclined to form an angle of 46° 40' with the *b* axis. If a row plane is defined as the plane passing through the *b* axis and parallel to the axes of the paraffin chains, then the angle between the row plane and the planes of the chains is 87° 30'. All dimers in a row are viewed as a single dimer in the (*h*0*l*) projection, as shown in the extended schematic (*h*0*l*) projection, Fig. 3(b). The perpendicular distance between the axes of adjacent chains in a row is (5.61 Å) (sin 46° 40') = 4.08 Å.

Since the attraction between paraffin chains is due to van der Waals interactions, the chains are expected

to be separated by a van der Waals 'thickness' of the chain. Assuming a C-H bond length of 1.09 Å, and

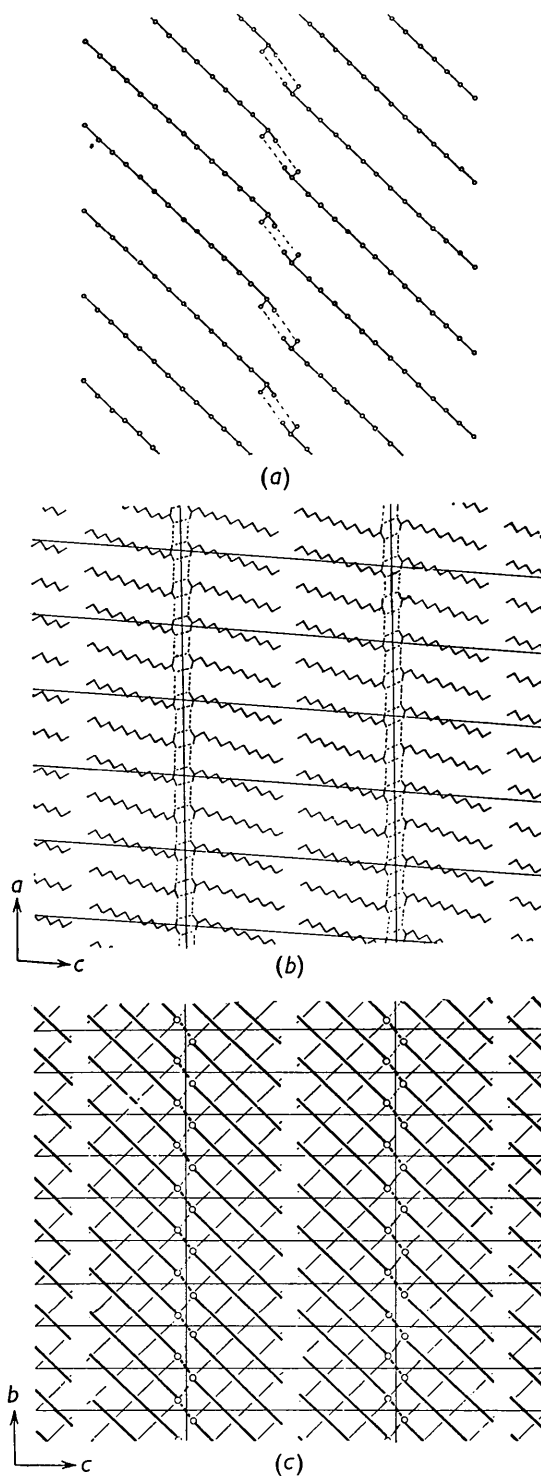


Fig. 3. (a) The packing of tetradecanamide dimers in a row, as viewed normal to the row plane.

(b) A schematic drawing of the (*h*0*l*) projection of tetradecanamide.

(c) A schematic drawing of the (0*kl*) projection of tetradecanamide.

H-C-H angle of 110° , and the van der Waals radius for hydrogen as suggested by Mack (1932), of 1.29 \AA , the thickness is found to be 4.37 \AA , appreciably larger than the observed distance between chains in tetradecanamide. If the tilt of the chains, relative to the b axis, is considered as an offsetting of the chains relative to one another, the distance of the offset in the direction of the chain axis is $(5.61 \text{ \AA}) (\cos 46^\circ 40') = 3.84 \text{ \AA}$. This distance is very nearly equal to $\frac{2}{3}$ the alternate carbon distance— 3.81 \AA . Thus, the n th carbon atom of one chain is closest to a point midway between the $(n+2)$ nd and the $(n+4)$ th carbon atoms of the preceding chain in the row. In such a position the hydrogen atom of the n th carbon atom may be in contact with the hydrogen atoms of both the $(n+2)$ nd and the $(n+4)$ th carbon atoms of the preceding chain. Assuming this arrangement, the effective thickness of the chain is calculated to be 4.03 \AA , which agrees well with the observed distance. A somewhat closer packing could be obtained if a hydrogen atom of the n th carbon atom came into contact with hydrogen atoms of the $(n+2)$ nd, $(n+3)$ rd and $(n+4)$ th carbon atoms. This would result in an effective chain thickness of about 3.93 \AA and an angle between the plane of chains and the row plane of 80° .

Schoon (1938) has suggested that paraffin chains will pack in those ways on which the atoms of one chain are closest to atoms of the adjacent chain. Since the n th atom of a chain may be closest to the n th, $(n+1)$ st, $(n+2)$ nd, etc. atom of the adjacent chain, several structures are possible in which the angle φ between the axis of the chain and the translation vector between the chains has values given by the relation:

$$\cos \varphi = (n \times 1.27 \text{ \AA}) / D,$$

where 1.27 \AA is the distance between the carbon atoms along the axis of the chain, n is the difference in number of the adjacent carbon atoms, and D is the distance between the chains, i.e. the effective thickness of the chains. Since n is integral, only discrete values of φ may occur, for a given value of D . This effect applies in the case of tetradecanamide. Using the theoretical distances and $n = 3$ in Schoon's equation, φ equals $46^\circ 37'$, which is effectively the angle observed.

The various possible tilts of paraffin chains should not, however, be viewed as those positions in which the carbon atoms are closest, but as those positions permitting the maximum van der Waals interactions between the hydrogen atoms of the adjacent chains. Further, it should be noted that the angle φ cannot necessarily be associated with either the axial angles of a monoclinic or triclinic cell, or the tilt expressed as the angle of the chain axis from the c^* direction.

The crystal structure is extended in the a direction, roughly normal to the row plane, by the addition of successive parallel rows of dimers to form a sheet of dimers two molecules thick, in which the chains of successive rows are tilted alternately in the positive

and negative b direction, as shown in the extended schematic $(0kl)$ projection, Fig. 3(c). Each dimer of a row is coupled by an N-H...O bond and an O...H-N bond to two adjacent dimers of the succeeding row. The centers of the dimers of a row are translated by $\frac{1}{2}b$ relative to the centers of the adjacent row. The a axis is in the plane of the centers, normal to the b axis. Further, to obtain optimum angles and distances for the hydrogen bonds between the rows, the rows are offset so that the angle between the row planes and the plane through the centers is $107^\circ 33'$.

The translation distance in the a direction must be the thickness of two rows. Since the chains of the adjacent rows are oppositely inclined there is no way that the hydrogen atoms of one row can be fitted into the hydrogen atoms of the adjacent row, and the effective thickness of a row should be the maximum van der Waals width of the chains, 4.70 \AA . The a translation should then be: $2(4.70 \text{ \AA}) / \sin 107^\circ 33' = 9.85 \text{ \AA}$. The observed a translation is 9.83 \AA .

The tilt of the chains in a paraffin compound is customarily expressed as the angle of tilt from the c^* direction. The tilt of the tetradecanamide chain is divided into components of $-17^\circ 33'$ toward the a axis and $\pm 44^\circ 40'$ toward the b axis, with a resultant tilt of $46^\circ 4'$. This resultant tilt is in good agreement with the tilt of $46^\circ 20'$ predicted from the variation of d_{001} with chain length for the even members of the n -aliphatic amide series (Turner & Lingafelter, 1955).

The crystal structure is extended in the c direction by the successive addition of the sheets of dimers. The surfaces of these sheets offer only the terminal methyl groups of the paraffin chains, so that the packing between the sheets will be a suitable van der Waals packing between the opposing methyl groups. Each methyl group is fitted into a space between four methyl groups of the opposite sheet, and closest to one methyl group related to it by a center of symmetry. The distance between the carbon atoms of these two methyl groups is 3.56 \AA , while the distance to the other three carbon atoms is about 4.6 \AA . The distance is appreciably greater than the minimum possible for two isolated methyl groups, about 3.1 \AA . However, by assuming the position observed in tetradecanamide the entire sheets may be packed closer together so that the distance between the opposing terminal carbon atoms in the c^* direction is only 2.1 \AA , while this distance between the sheets would be about 2.6 \AA , if the two methyl groups were placed at the minimum distance from each other.

General

In the crystal structure of tetradecanamide, the dimers are held together by both the van der Waals interactions between the chains and by the hydrogen-bond system. The large increase in the stability of the tetradecanamide structure due to the hydrogen bond system is shown by the increase of the melting point

of tetradecanamide as compared to tetradecane ($\Delta T = 100^\circ \text{C.}$), where no hydrogen-bond system is possible, and to tetradecanoic acid ($\Delta T = 51^\circ \text{C.}$), where only a one-dimensional system is possible. The crystal growth of tetradecanamide is much larger in the a and b directions than in the c direction, where the only attraction between the sheets of dimers is the van der Waals interaction between the terminal methyl groups. The weak attraction between sheets also introduces the observed cleavage along the (001) plane. The crystals also show a cleavage along an ($h0l$) plane whose indices have not been determined owing to the thinness of the crystals, but which is probably a cleavage between the rows of dimers.

The arrangement of the paraffin chains in tetradecanamide is quite similar to the structure reported for form A of potassium caprate (Vand, Lomer & Lang, 1949). In both compounds the paraffin chains are tilted strongly in the b direction, with successive rows in the a direction oppositely inclined. However, there is a striking difference in the orientation of the planes

of the chains. In the tetradecanamide the planes of the chains are nearly parallel to the a axis, while in potassium caprate they are reported to be more nearly normal to the a axis.

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On the Structure of the Crystal Form B of Stearic Acid

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Form B of stearic acid, $\text{C}_{17}\text{H}_{35}\text{COOH}$, is monoclinic with $a = 5.591$, $b = 7.404$, $c = 49.38 \text{ \AA}$ and $\beta = 117^\circ 22'$. The cell contains four molecules. The space group is $C_{2h}^2-P2_1/a$. The packing of the hydrocarbon chains is of the common orthorhombic type. The hydrocarbon chains are deformed near the carboxylic groups.

Introduction

The crystalline B -form of normal fatty acids with an even number of carbon atoms was first investigated with X-rays by Müller (1927). He determined the unit-cell dimensions and the space group of the B -form of stearic acid and made a very promising start in calculating the crystal structure. As no continuation of his work appeared, the problem has been taken up in Uppsala as a part of an investigation of the crystal behaviour of normal fatty acids (see Stenhagen & von Sydow (1953), von Sydow (1954*a*, *b*), and Abrahamsson & von Sydow (1954)). Thibaud & Dupré La Tour (1932) redetermined the unit cell of form B with X-rays and Trillat & v. Hirsch (1932) the smallest axis-plane with electron diffraction. Verma (1955) has determined the unit-cell dimensions of the B -form of palmitic acid.

Preparation of crystals

The very pure stearic acid used was prepared by Prof. E. Stenhagen and his collaborators. It has a melting point of 69.7°C. Francis & Piper (1939) found for the same acid 69.6°C.

According to Müller (1927), the B -form of stearic acid crystallizes from carbon disulfide, and according to Stenhagen & von Sydow (1953) and others it crystallizes together with the C -form from petroleum (b.p. $40\text{--}60^\circ \text{C.}$). If large quantities are used, formation of the B -form is favoured, and in this way large crystals of this form were obtained.

The crystals grew in rhombic plates having an acute angle of 74° . Müller (1927) found the same value. Investigation in polarized light revealed that twinning was very common among the crystals. In one case X-ray photographs had to be taken before twinning