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The Crystal Structure of Decanamide

BY J. R. BRATHOVDE AND E. C. LINGAFELTER

Department of Chemistry, University of Washington, Seattle 5, Washington, U.S.A.

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The crystal structure of decanamide, $CH_3(CH_2)_8CONH_2$, has been determined by two-dimensional projections. Individual atom anisotropic temperature factors have been included and the final values of R are $R_{h0l} = 0{\cdot}091$ and $R_{0kl} = 0{\cdot}097$. The structure is quite similar to that of tetradecanamide.

Introduction

As a continuation of the study of the *n*-aliphatic amides (Turner & Lingafelter, 1955*a*, *b*), the crystal structure of decanamide, $CH_3(CH_2)_8CONH_2$, has been determined by two-dimensional projections. The diffraction pattern of decanamide differs from that of tetradecanamide (Turner & Lingafelter, 1955*b*) in that the (200) reflection is the center one of the three intense spots in the (20*l*) row rather than an outside one (Turner & Lingafelter, 1955*a*). Furthermore, our treatment of the data differs in that, for decanamide, we have used McWeeny scattering factors, have included the contributions of the hydrogen atoms, and have introduced individual anisotropic temperature factors for the *h*0*l* zone, thus giving much more complete refinement.

Experimental

Decanamide crystallizes by evaporation of the solvent from *n*-butyl acetate solutions at room temperature in thin monoclinic tablets with prominent (001) faces. One lath-like crystal, elongated in the **b** direction (0·12×0·16×3·0 mm.), was found in a batch of crystals grown by Turner (Turner & Lingafelter, 1955*a*). This crystal was used for all photographs taken with rotation about **b**. Another large crystal (0·5×10×10 mm.), grown by very slow (30 days) evaporation, was made into a cylindrical rod (0·14×2·0 mm.) elongated in the **a** direction, by cutting it to size and dipping it repeatedly into the solvent. This crystal was used to obtain (0*kl*) data.

Interpretation of equi-inclination Weissenberg photographs taken with copper radiation ($\lambda = 1{\cdot}5418$ Å) gave the following results:

$$a_0=9{\cdot}830\pm0{\cdot}013,\ b_0=5{\cdot}555\pm0{\cdot}003,\ c_0=21{\cdot}224\pm0{\cdot}033\ \text{Å},\quad \beta = 103^\circ\ 27'\pm6'.$$

(*h*0*l*) absent for *h* odd, (0*k*0) absent for *k* odd; probable space group: $P2_1/a$–C_{2h}^5.

Number of molecules per cell = 4. Density, calc. 1·010 g.cm.$^{-3}$, obs. 1·006 g.cm.$^{-3}$ (Turner & Lingafelter, 1955*a*).

Photographs for intensity measurement were prepared and photometered as previously described (Turner & Lingafelter, 1955*b*) but the area under the photometer tracing for each reflection was determined with a linear-to-log converter and integrator (Brathovde & Breazeale, 1955) and this area was taken to be equal to the relative intensity. The precision of the determination of intensities was found to be 4·5% for 94 reflections which appeared on more than one film.

177 (*h*0*l*) and 97 (0*kl*) reflections out of a possible 218 and 146, respectively, were measured, giving a range of 1 to 12000 in relative intensity. Lorentz and polarization factors were applied, but no correction was made for absorption.

Structure factors were calculated using McWeeny scattering factors (McWeeny, 1951) and, for the *h*0*l* zone, individual anisotropic temperature factors in the form $\exp\,[-(A_i+C_i\cos^2\varphi_i)\sin^2\theta/\lambda^2]$, where A_i and C_i are characteristic of the atom and φ_i is the angle between the direction of maximum vibration and the normal to the reflection plane. For the 0*kl* zone, because of the uncertainties due to lack of resolution, individual isotropic temperature factors were used. The final values of the temperature-factor parameters are given in Table 1.

Table 1. *Temperature factor parameters*

	*h*0*l*		0*kl*
Atom	A_i	C_i	B_i
N	2·2	1·8	4·0
O	1·5	2·9	4·4
C_1	2·4	1·2	3·6
C_2	2·6	1·2	3·8
C_3	3·0	1·0	4·0
C_4	3·6	0	3·6
C_5	3·6	0	3·6
C_6	3·8	0	3·8
C_7	4·8	0	4·8
C_8	5·4	0	5·4
C_9	5·8	1·5	6·0
C_{10}	7·5	1·1	7·6

All atoms have direction of maximum vibration parallel to c^* except C_9 and C_{10}, for which it is 70° from c^*.

In all cases each hydrogen atom was given a temperature factor equal to that of the carbon or nitrogen atom to which it is attached. The calculations were carried out on the IBM Type-604 Calculator. Refinements of atomic positions were made from differential difference syntheses (Cochran & Lipson, 1953) calculated on the 604. Refinements of temperature factors were made from difference syntheses calculated on the 604 and the IBM Type-407 Tabulator. The final set of F's, given in Table 3, were calculated on the IBM Type-650.

Determination of the structure

Trial structures for both projections (i.e., on (100) and on (010)) were assumed by analogy with the structure of tetradecanamide, and the two projections were refined completely independently.

For the projection on (010), in which all atoms are resolved, hydrogen atom contributions were included at $R = 0\cdot252$, where $R = \Sigma||F_o|-|F_c|| \div \Sigma|F_o|$, omitting unobserved terms; the hydrogen atom positions were not further refined, but were recalculated after the last refinement and before the calculation of the final set of F's. In calculating the hydrogen atom positions, C–H was taken as 1·075 Å and N–H as 1·005 Å. Individual atomic anisotropic temperature factors were introduced at $R = 0\cdot202$. From this point the refinement proceeded by alternate use of differential difference and difference syntheses. This procedure reduced R to a final value of 0·107.

Fig. 1 shows clearly the necessity for individual temperature factors by the progressive broadening and lowering of the electron-density peaks away from the amide end of the molecule. Fig. 2, a difference synthesis calculated with isotropic temperature factors, shows the anisotropy which necessitates the use of anisotropic temperature factors.

While the individual anisotropic temperature factors are clearly necessary to give good agreement between calculated and observed structure factors, we have not, as yet, determined how much difference, if any, their use may make in the final atomic positions.

Owing to the crossed-chain arrangement (Turner & Lingafelter, 1955*b*) in the projection on (100), only 6 of the 12 heavy atoms (C, N, and O) are resolved. This makes both positions and temperature factors more difficult to determine and of lower accuracy because of the mutual interaction of the several effects. This projection was refined by essentially the same procedure as for the previous projection, giving a final value of $R = 0\cdot089$.

At this point the two projections were compared and a weighted average set of final parameters and temperature factors was calculated. These final parameters, which give $R_{h0l} = 0\cdot091$ and $R_{0kl} = 0\cdot097$ are listed in Table 2. The complete list of observed and calculated structure factors is given in Table 3.

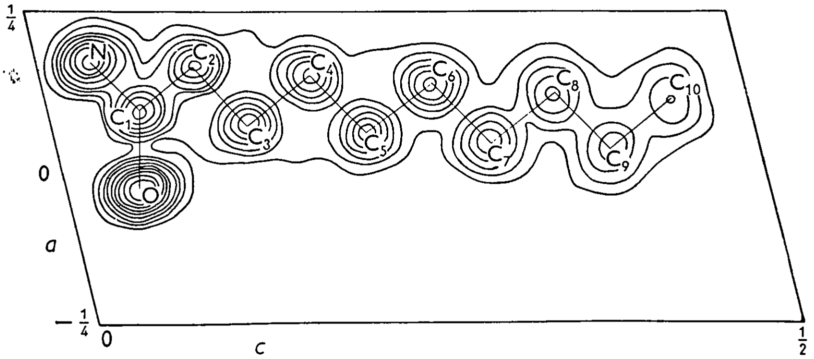

Fig. 1. Electron-density projection on (010). Contours at 1 e.Å^{-2}. Zero contour and 1 e.Å^{-2} contours omitted.

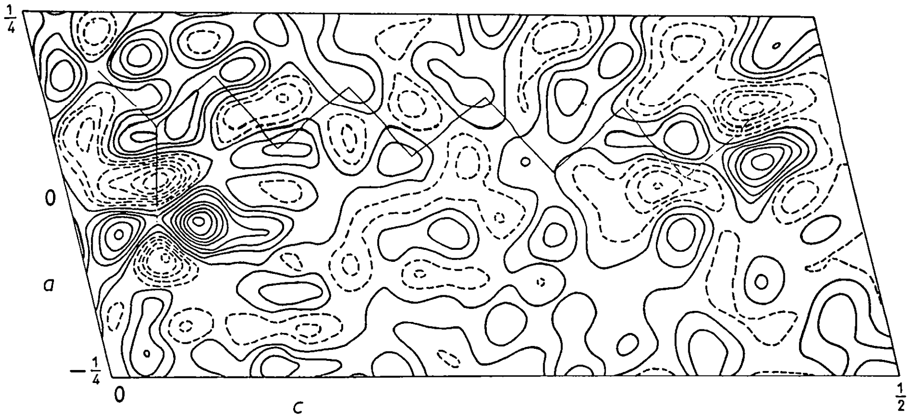

Fig. 2. Difference synthesis projection on (010). Contours at $\frac{1}{8}$ e.Å^{-2}. Negative contours broken.

Table 2. *The atomic coordinates and their standard deviations*

Nitrogen, oxygen and carbon atoms

Atom	x/a	y/b	z/c	$\sigma(x)$ Å	$\sigma(y)$ Å	$\sigma(z)$ Å
N_{11}	0·1711	0·1460	0·0375	0·0045	0·008	0·0051
O_{12}	−0·0380	0·2243	0·0507	0·0035	0·008	0·0048
C_1	0·0917	0·2827	0·0645	0·0047	0·010	0·0055
C_2	0·1639	0·4682	0·1096	0·0057	0·010	0·0062
C_3	0·0663	0·6095	0·1384	0·0060	0·010	0·0058
C_4	0·1481	0·7801	0·1913	0·0067	0·010	0·0061
C_5	0·0530	0·9471	0·2223	0·0066	0·010	0·0059
C_6	0·1346	0·1110	0·2760	0·0067	0·012	0·0062
C_7	0·0369	0·2619	0·3075	0·0087	0·017	0·0079
C_8	0·1203	0 4208	0·3624	0·0131	0·017	0·0090
C_9	0·0237	0·5737	0·3925	0·0143	0·017	0·0100
C_{10}	0·1100	0·7397	0·4446	0·0218	0·025	0·0127

Hydrogen atoms

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
H_{13}	0·125	0·017	0·007	H_{24}	0·200	0·001	0·313
H_{14}	0·272	0·191	0·042	H_{25}	−0·027	0·375	0·271
H_{15}	0·217	0·588	0·084	H_{26}	−0·029	0·143	0·327
H_{16}	0·239	0·382	0·148	H_{27}	0·188	0·537	0·343
H_{17}	0·000	0·714	0·101	H_{28}	0·182	0·307	0·399
H_{18}	0·004	0·489	0·160	H_{29}	−0·042	0·681	0·356
H_{19}	0·215	0·892	0·170	H_{30}	−0·040	0·458	0·414
H_{20}	0·211	0·672	0·229	H_{31}	0·174	0·855	0·423
H_{21}	−0·008	0·058	0·185	H_{32}	0·176	0·632	0·482
H_{22}	−0·015	0·835	0·243	H_{33}	0·042	0·848	0·466
H_{23}	0·199	0·231	0·256				

Table 3. *Observed and calculated structure factors*

Values are multiplied by 10

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	$F_{obs.}$	$F_{calc.}$	hk l	$F_{obs.}$	$F_{calc.}$
00 0	----	3840	40 7	129	116	100 5	39	41	$\bar{4}$017	100	112	$\bar{8}$017	<30	-22	02 6	<20	16	0410	59	54
00 1	567	532	40 8	90	86	100 6	30	30	$\bar{4}$018	100	96	$\bar{8}$018	<30	-25	02 7	59	72	0411	<30	-7
00 2	<10	-3	40 9	60	12	100 7	<20	27	$\bar{4}$019	60	74	$\bar{8}$019	30	-37	02 8	521	531	0412	<30	6
00 3	309	309	4010	<30	11	100 8	<20	19	$\bar{4}$020	70	70	$\bar{8}$020	39	-39	02 9	197	218	0413	<30	26
00 4	160	-143	4011	139	-146	120 0	<10	-3	$\bar{4}$021	<30	-3	$\bar{8}$021	<20	-36	0210	176	173	0414	<30	-33
00 5	70	59	4012	229	227	120 1	10	70	$\bar{4}$022	60	-46	$\bar{8}$022	30	-40	0211	59	74	0415	<30	-10
00 6	258	-251	4013	199	194	120 2	10	62	$\bar{4}$023	109	109	$\bar{8}$023	30	-55	0212	69	64	0416	59	85
00 7	170	-156	4014	139	-157	$\bar{2}$0 1	1095	1126	$\bar{4}$024	70	83	$\overline{10}$0 1	90	-75	0213	<20	35	0417	49	58
00 8	289	-274	4015	119	-106	$\bar{2}$0 2	60	43	$\bar{6}$0 1	60	40	$\overline{10}$0 2	100	-100	0214	<30	30	0418	30	25
00 9	249	-255	4016	100	-103	$\bar{2}$0 3	498	521	$\bar{6}$0 2	39	-21	$\overline{10}$0 3	90	-91	0215	49	-48	0419	30	32
0010	199	-195	4017	39	-62	$\bar{2}$0 4	90	-102	$\bar{6}$0 3	80	-70	$\overline{10}$0 4	90	-94	0216	157	-143	0420	49	37
0011	189	-200	4018	30	-43	$\bar{2}$0 5	199	195	$\bar{6}$0 4	129	-113	$\overline{10}$0 5	60	-80	0217	<30	-13	0421	20	-15
0012	398	-375	4019	<30	-25	$\bar{2}$0 6	149	-151	$\bar{6}$0 5	139	-142	$\overline{10}$0 6	60	-70	0218	<30	47	05 1	<30	8
0013	100	-111	60 0	139	150	$\bar{2}$0 7	<20	-32	$\bar{6}$0 6	129	-121	$\overline{10}$0 7	49	-55	0219	<30	6	05 2	39	-21
0014	<30	-21	60 1	90	81	$\bar{2}$0 8	160	-152	$\bar{6}$0 7	90	-106	$\overline{10}$0 8	<30	-26	0220	30	-58	05 3	69	-58
0015	<60	-7	60 2	70	38	$\bar{2}$0 9	70	-78	$\bar{6}$0 8	49	-53	$\overline{10}$0 9	90	-67	03 1	30	46	05 4	98	-94
0016	60	45	60 3	170	183	$\bar{2}$010	80	-93	$\bar{6}$0 9	60	-79	$\overline{10}$010	109	-96	03 2	107	113	05 5	49	51
0017	<30	27	60 4	170	138	$\bar{2}$011	139	-117	$\bar{6}$010	309	332	$\overline{10}$011	60	59	03 3	79	102	05 6	49	64
0018	49	61	60 5	170	162	$\bar{2}$012	49	40	$\bar{6}$011	139	140	$\overline{10}$012	129	120	03 4	148	163	05 7	<30	15
0019	<30	29	60 6	129	103	$\bar{2}$013	39	45	$\bar{6}$012	249	-255	$\overline{10}$013	90	89	03 5	79	87	05 8	<30	13
0020	30	30	60 7	90	96	$\bar{2}$014	70	69	$\bar{6}$013	109	-81	$\overline{10}$014	90	91	03 6	118	117	05 9	<30	10
0021	<30	14	60 8	60	41	$\bar{2}$015	60	58	$\bar{6}$014	80	-62	$\overline{10}$015	70	68	03 7	20	19	0510	39	21
0022	49	64	60 9	<30	7	$\bar{2}$016	90	79	$\bar{6}$015	39	-17	$\overline{10}$016	60	62	03 8	59	65	0511	<30	26
0023	<30	-3	6010	49	-31	$\bar{2}$017	39	56	$\bar{6}$016	<30	1	01 1	157	-144	03 9	<59	-29	0512	30	22
0024	60	-78	6011	<30	-26	$\bar{2}$018	70	60	$\bar{6}$017	<30	5	01 2	49	-81	0310	59	85	0513	30	10
20 0	707	711	6012	60	65	$\bar{2}$019	<30	36	$\bar{6}$018	<30	18	01 3	216	-206	0311	59	-50	0514	30	9
20 1	1165	-1224	6013	160	-170	$\bar{2}$020	39	24	$\bar{6}$019	<30	3	01 4	1278	-1323	0312	364	-340	0515	30	27
20 2	209	-198	6014	209	-213	$\bar{2}$021	<30	-33	$\bar{6}$020	<30	20	01 5	452	-445	0313	<30	-51	0516	30	28
20 3	160	-157	6015	90	-87	$\bar{2}$022	<30	33	$\bar{6}$021	<30	10	01 6	295	-288	0314	<30	8	0517	30	-33
20 4	90	-86	6016	49	-51	$\bar{2}$023	109	95	$\bar{6}$022	70	-76	01 7	255	-271	0315	<30	-13	0518	20	-6
20 5	100	-106	80 0	109	-76	$\bar{2}$024	80	-76	$\bar{6}$023	<20	-36	01 8	383	-367	0316	<30	9	06 0	79	-78
20 6	109	-104	80 1	199	-205	$\bar{2}$025	80	-107	$\bar{6}$024	60	53	01 9	39	-79	0317	<30	0	06 1	<20	18
20 7	139	-129	80 2	39	-22	$\bar{2}$026	39	-53	$\bar{6}$025	30	32	0110	79	69	0318	<30	18	06 2	<20	32
20 8	119	-111	80 3	109	106	$\bar{4}$0 1	<20	18	$\bar{8}$0 1	60	-65	0111	49	46	0319	<20	14	06 3	30	-7
20 9	160	-163	80 4	60	59	$\bar{4}$0 2	229	-214	$\bar{8}$0 2	90	-90	0112	128	127	0320	<20	18	06 4	<20	12
2010	49	-57	80 5	70	78	$\bar{4}$0 3	149	-125	$\bar{8}$0 3	90	-82	0113	79	98	0321	<20	21	06 5	<20	-4
2011	328	-328	80 6	60	49	$\bar{4}$0 4	299	-279	$\bar{8}$0 4	100	-90	0114	89	94	0322	<20	-21	06 6	<20	4
2012	189	-194	80 7	39	48	$\bar{4}$0 5	209	-211	$\bar{8}$0 5	90	-77	0115	49	67	0323	<20	12	06 7	<20	7
2013	289	282	80 8	<30	6	$\bar{4}$0 6	249	-226	$\bar{8}$0 6	70	-61	0116	138	147	0324	49	64	06 8	30	15
2014	109	82	80 9	<30	-3	$\bar{4}$0 7	180	-195	$\bar{8}$0 7	<30	-34	0117	39	58	04 0	69	75	06 9.	30	20
2015	60	58	8010	<30	-15	$\bar{4}$0 8	170	-171	$\bar{8}$0 8	<30	4	0118	49	57	04 1	30	42	0610	<20	2
2016	30	35	8011	<30	-3	$\bar{4}$0 9	160	-139	$\bar{8}$0 9	80	-79	0119	<30	-9	04 2	49	39	0611	<20	-1
40 0	209	-195	8012	39	-32	$\bar{4}$010	70	62	$\bar{8}$010	149	128	0120	79	-84	04 3	<20	-17	0612	20	16
40 1	49	-18	8013	80	-69	$\bar{4}$011	348	-367	$\bar{8}$011	379	403	02 0	324	-319	04 4	<30	4	07 1	<10	12
40 2	189	148	100 0	139	-112	$\bar{4}$012	219	-206	$\bar{8}$012	199	174	02 1	207	-199	04 5	39	-21	07 2	<10	-29
40 3	209	209	100 1	<30	-42	$\bar{4}$013	90	-63	$\bar{8}$013	70	91	02 2	285	-281	04 6	49	-37	07 3	20	-37
40 4	219	206	100 2	160	165	$\bar{4}$014	70	75	$\bar{8}$014	70	70	02 3	157	-158	04 7	89	-98	07 4	20	20
40 5	209	202	100 3	139	111	$\bar{4}$015	109	117	$\bar{8}$015	<30	25	02 4	314	-298	04 8	186	-162			
40 6	180	172	100 4	39	35	$\bar{4}$016	119	117	$\bar{8}$016	<30	17	02 5	79	65	04 9	59	55			

Discussion

The structure of decanamide does not differ appreciably from that of tetradecanamide except for the length of the *c* axis and the details of the packing of the methyl groups, both caused by the difference of chain length. Table 4 compares the two structures quantitatively.

Table 4. *Comparison of decanamide and tetradecanamide*

Values in the table are coordinates of atoms on the orthogonal set of axes *a*, *b*, and *c**

	x (Å)		y (Å)		z (Å)	
	C_{10}	C_{14}	C_{10}	C_{14}	C_{10}	C_{14}
N	1·4968	1·4891	0·8112	0·8184	0·7741	0·8025
O	−0·6238	−0·6208	1·2462	1·3871	1·0466	1·0616
C_1	0·5830	0·5572	1·5707	1·5498	1·3314	1·3374
C_2	1·0700	1·0683	2·6013	2·5588	2·2624	2·2765
C_3	−0·0315	−0·0368	3·3864	3·3710	2·8568	2·8700
C_4	0·5114	0·4903	4·3009	4·3537	3·9488	3·9707
C_5	−0·5764	−0·5964	5·2621	5·2747	4·5887	4·5781
C_6	−0·0394	−0·0768	6·1727	6·1217	5·6971	5·7205
C_7	−1·1553	−1·1710	7·0589	6·9883	6·3474	6·3558
C_8	−0·6066	−0·6470	7·8940	7·8941	7·4806	7·4816
C_9	−1·7047	−1·7432	8·7435	8·7472	8·1019	8·1168
C_{10}	−1·1136	−1·2124	9·6658	9·6110	9·1774	9·2759
C_{11}	—	−2·3078	—	10·4855	—	9·9363
C_{12}	—	−1·8293	—	11·3010	—	11·0537
C_{13}	—	−2·8844	—	12·1098	—	11·7698
C_{14}	—	−2·3474	—	13·0078	—	12·8704

The bond distances and angles for decanamide are listed in Table 5, along with the standard deviations calculated by the method of Cruickshank (1949). The curvatures used in the calculations were measured on the final Fourier maps. The curvatures of the carbon atoms range from 84 e.Å^{-4} at the amide end of the paraffin chain to 18 e.Å^{-4} at the methyl end. Owing to the difficulties arising from overlap of atoms in the projection on (100), we feel that the **y** coordinates are less accurate than indicated by σ.

Table 5. *Bond lengths and standard deviations, and bond angles*

Bond lengths

	d (Å)	σ (Å)
C_1–C_2	1·472	0·010
C_2–C_3	1·478	0·010
C_3–C_4	1·545	0·011
C_4–C_5	1·566	0·011
C_5–C_6	1·532	0·011
C_6–C_7	1·540	0·014
C_7–C_8	1·538	0·018
C_8–C_9	1·521	0·019
C_9–C_{10}	1·535	0·024
N–C_1	1·312	0·009
O–C_1	1·282	0·009
N–H · · · O	2·88 (intradimer)	
N–H · · · O	2·90 (interdimer)	

Bond angles

N–C_1–O	114·4°	C_4–C_5–C_6	113·9°
N–C_1–C_2	116·3	C_5–C_6–C_7	112·0
O–C_1–C_2	129·0	C_6–C_7–C_8	111·4
C_1–C_2–C_3	112·3	C_7–C_8–C_9	111·3
C_2–C_3–C_4	110·4	C_8–C_9–C_{10}	110·1
C_3–C_4–C_5	114·1		

The average C–C bond length (omitting C_1–C_2 and C_2–C_3) is 1·540 Å (σ = 0·014) which may be compared with the value of 1·534 Å reported by Shearer & Vand (1956) for *n*-hexatriacontane. The average C–C–C bond angle is 111·9° (σ = 45′) (cf. 112° 1′ for *n*-hexatriacontane). The N–H · · · O hydrogen bond distances are somewhat shorter than those found in tetradecanamide, but the two values for decanamide are essentially equal.

The shortening of the C_1–C_2 bond is not surprising, owing to the interaction with the amide group. However, we have no explanation for the shortness of the C_2–C_3 bond.

As another test, (0*kl*) structure factors were calculated for an assumed structure in which the **y** coordinates of those atoms which were unresolved in the projection were adjusted so as to give the best possible agreement of bond lengths with those generally quoted in the literature. This calculation gave R = 0·133.

From a comparison of the structures of tetradecanamide, decanamide, and pentanamide (Adamsky & Lingafelter, 1958), it does not appear to be possible to explain the methyl group packing, and therefore the values of β, without consideration of the positions of the hydrogen atoms. This must therefore await three-dimensional investigations.

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References

ADAMSKY, R. A. & LINGAFELTER, E. C. (1958). (unpublished.)

BRATHOVDE, J. R. & BREAZEALE, J. D. (1955). *Rev. Sci. Instrum.* **26**, 892.

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

CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **5**, 644.

MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.

SHEARER, H. M. M. & VAND, V. (1956). *Acta Cryst.* **9**, 379.

TURNER, J. D. & LINGAFELTER, E. C. (1955*a*). *Acta Cryst.* **8**, 549.

TURNER, J. D. & LINGAFELTER, E. C. (1955*b*). *Acta Cryst.* **8**, 551.