

## The X-ray Crystallography of the *n*-Aliphatic Amides

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(Received 23 August 1954 and in revised form 14 February 1955)

The unit-cell dimensions and space groups of the *n*-aliphatic amides, from propanamide through tetradecanamide, and hexadecanamide have been determined. All of the compounds studied have essentially the same structure, as shown by the constancy of the  $a_0$  (9.8 Å) and  $b_0$  (5.6 Å) cell dimensions and the intensity distribution in the diffraction patterns. Minor variations in the crystal structures were found, but no single property was found which could be correlated with the irregularities in the melting points of the series.

### Introduction

For several years investigations have been conducted in this laboratory on the crystal structures and the behavior of various series of paraffin chain compounds. It was noted that the melting points of the *n*-aliphatic amides, as reported by Ralston (1948), vary irregularly with chain length rather than following the usual homologous series pattern. An investigation was undertaken to determine, if possible, whether this behavior was reflected in the crystal structures of the *n*-aliphatic amides.

### Experimental

All of the amides studied, except hendecanamide and tridecanamide, which were obtained from Prof. J. Cason, University of California, were prepared from the Eastman White Label aliphatic acids. Propanamide and pentanamide were prepared by making the acyl bromides from the acids and treating these with ammonia. These amides were then purified by recrystallization from benzene. Butanamide, hexanamide through decanamide, tetradecanamide, and

hexadecanamide were prepared by passing a stream of dry ammonia through the acid at 190–210° C. for 10–14 hr., as described by Ralston (1948). These compounds were then purified by recrystallizations from acetone. The corrected melting points of the final products were then compared with those reported by Ralston and found to agree satisfactorily (see Table 1).

Crystals for the X-ray study were grown from a variety of solvents. They were, in general, lath-like in form with prominent {001} faces. The side faces are usually {*h*0*l*} planes whose indices could not be determined owing to the thinness of the crystals. The ends of the lathes are irregular. The crystals show not only the cleavage along the {001} plane usually found in long chain compounds, but also a cleavage along an {*h*0*l*} plane whose indices, again, could not be determined owing to the thinness of the crystals.

Propanamide crystals were grown from the molten amide by slowly cooling the melt, and formed long tabular crystals.

Butanamide crystals were obtained as flat needles by the evaporation of a benzene solution.

Pentanamide crystals were grown as needles by the evaporation of a *n*-hexane solution, and as long tablets by the evaporation of a nitroethane solution.

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Table 1. *Physical constants of the n-aliphatic amides*

Compound	M. p.* (°C.)	M. p. (obs.) (°C.)	$a_0$ (Å)	$b_0$ (Å)	$c_0$ (Å)	$\beta$ (°)	$d$ (obs.) (g.cm. <sup>-3</sup> )	$d$ (calc.) (g.cm. <sup>-3</sup> )	Cross section (Å <sup>2</sup> )
Propanamide	77	78	9.76	5.78	8.97	113.5	1.046	1.046	20.57
Butanamide	115	113–113.5	9.94	5.79	10.02	100.9	1.027	1.006	19.87
Pentanamide	106	105	9.84	6.13	11.08	100.7	1.032	1.024	21.99
Hexanamide	101	99.4–99.6	9.78	5.65	14.11	101.6	0.990	1.002	19.07
Heptanamide	96.1	95	9.90	5.65	15.29	105.0	1.028	1.038	20.42
Octanamide	105.9	104.9–105.3	9.78	5.69	17.39	91.9	0.972	0.983	19.19
Nonanamide	98.8	98.5–99.0	9.86	5.59	39.15	103.8	0.993	0.996	20.11
Decanamide	98.5	98.0–98.5	9.83	5.56	21.23	103.8	1.006	1.010	18.85
Hendecanamide	99	98.0–98.7†	9.85	5.59	21.96	92.8	1.012	1.019	20.09
Dodecanamide	102.4	101.7–102.0	9.83	5.57	25.10	103.4	0.996	0.991	18.89
Tridecanamide	100	99.2–100.4†	9.79	5.59	25.90	93.8	0.998	1.002	19.97
Tetradecanamide	105.1	103.5–104.5	9.83	5.61	27.98	95.1	0.984	0.983	19.04
Pentadecanamide	—	—	—	—	—	—	—	—	—
Hexadecanamide	107	104	9.84	5.54	31.44	93.4	1.000	0.993	18.80

\* Ralston (1948). † Cason & Winans (1950).

Hexanamide crystals were obtained from the evaporation of a 50% alcohol-water solution as flakes, much like feathers in form.

Heptanamide crystals were obtained as thin needles by the slow cooling of an aqueous solution.

Octanamide, nonanamide, decanamide and dodecanamide crystals were grown by slowly cooling *n*-butyl acetate solutions. All these formed thin flakes.

Tetradecanamide crystals, in the form of tablets, were obtained from a slowly cooled aqueous solution.

Hexadecanamide crystals were grown from an alcoholic solution as fine needles.

The crystals of hendecanamide and tridecanamide were taken directly from the samples furnished by Prof. Cason, the former being in the form of fine needles and the latter, tablets. Although these crystals were small and poorly formed, no attempt was made to grow better crystals of these compounds.

Single crystals of each of the members of the series, propanamide through tetradecanamide, and hexadecanamide were selected and their X-ray diffraction patterns were obtained by means of oscillation, rotation, equi-inclination Weissenberg, and precession photographs using Cu *K*α ( $\lambda = 1.5418 \text{ \AA}$ ) radiation. The effective diameter of the Weissenberg camera was found to be 57.074 mm. by calibration with sodium chloride.

### Results

Examination of the X-ray photographs showed all members of the series to have Laue symmetry  $2/m-C_{2h}$ . Systematic absences were (*h*0*l*) for *h* odd and (0*k*0) for *k* odd. Nonanamide (only), with  $c_0$  twice as large as for the other members of the series, also showed (*hkl*) absent for *k*+*l* odd. The space group for nonanamide is therefore  $Aa-C_s^4$  or  $A2/a-C_{2h}^2$  and the space group for the other members of the series is  $P2_1/a-C_{2h}^2$ .

The unit-cell dimensions determined from the rotation and zero-level Weissenberg photographs for each compound are listed in Table 1. The values listed are the averages, weighted according to order, of all pertinent spacings measured.

The density of each compound was computed from the unit-cell dimensions, assuming eight molecules per unit cell for nonanamide and four molecules per unit cell for the other members of the series. The calculated densities and the observed densities, experimentally determined by the flotation method, are given in Table 1.

### Discussion

It may be seen from the table that  $a_0$  is approximately 9.8 Å in all cases, and, except for pentanamide,  $b_0$  is approximately 5.6 Å. Taking  $\frac{1}{2}c_0$  for nonanamide, the  $c_0$ 's vary continuously with chain length. Further, the diffraction patterns of all the amides are very similar in distribution of intensity. In particular, there are three adjacent, very intense reflections in the

(20*l*) row of the (*h*0*l*) net. The center reflection of the three is located about 103° from the  $c^*$  axis in all cases. In the (0*kl*) nets there is a reflection, or pair of reflections, of high intensity in the (01*l*) row, located about 45° from the  $c^*$  axis in all cases. In the structure of tetradecanamide (Turner & Lingafelter, 1955) these reflections were found to be directly related to the tilt of the paraffin chains in the respective projections. It may then be reasonably concluded that the crystal structures of all the compounds studied are essentially the same, nonanamide differing from the others only by the *A* centering.

From the variation of  $d_{001}$  with chain length, and assuming a distance of 2.54 Å between alternate carbon atoms in the chain direction, the average tilt of the chains from the  $c^*$  direction was found to be 43° 8' for the odd members of the series, and 46° 20' for the even members of the series. The tilt of the tetradecanamide chain was found, from the structure determination, to be 46° 4' (Turner & Lingafelter, 1955).

The efficiency of packing of the paraffin chains may be expressed by the cross-section, i.e. the cross-sectional area per chain normal to the chain direction,  $\sigma = \frac{1}{2}a_0b_0 \cos(\text{tilt})$ . These values are listed in Table 1 for each compound, and are seen to be near 19.0 Å<sup>2</sup> for the even members of the series and near 20.0 Å<sup>2</sup> for the odd members of the series. The cross-section of pentanamide is distinctly higher than for the other odd members of the series and the cross-section of butanamide is higher than for the other even members of the series, yet the melting points of pentanamide and butanamide are the highest of the odd and even members of the series, respectively, despite the looser packing indicated by the higher cross-sections.

The constancy of the position of the middle reflection of the three characteristic reflections of the (20*l*) row suggests the choice of this direction as a natural  $a^*$  axis direction, which could be related to the crystal structures of the series. However, it was found that this direction is a possible choice in only about half the cases. Since there is no corresponding variation in the intensity distribution of the patterns, the amide molecules must be all oriented in the same way, but with some variation in the packing between methyl groups of successive molecules in the *c* direction, as indicated by the variation in possible axial directions. This variation is neither an alternation, which could be related to odd- and even-numbered carbon chains, nor does it appear to have any relation to the variations in melting points. Further study of this variation is in progress.

### References

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