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A Refinement of the Crystal Structure of Succinamide*

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The structure of succinamide has been refined to a high degree of precision by three-dimensional Fourier and least-squares methods. In this structure the molecules are planar and are tied into layers by a net of hydrogen bonds. The bond lengths in the amide group are C-N = 1.333 and C-O = 1.238 Å; the bond angles are C-C-N = 115° 36', C-C-O = 122° 23', and N-C-O = 122° 2'. The two non-equivalent C-C bonds have lengths of 1.512 and 1.501 Å, the central bond being slightly but significantly longer.

Introduction

When the crystal-structure determination of succinamide was initiated, the dimensions of the terminal amide group had been determined in only three compounds: acetamide (Senti & Harker, 1940), glutamine (Cochran & Penfold, 1952) and glycy lasparagine (Pasternak, Katz & Corey, 1954). Because the bond lengths and angles reported for this group in these three investigations differed significantly, a precise determination of the succinamide structure, which is simpler than any of the other three, was considered to be of value. Recently, the crystal structures of formamide (Ladell & Post, 1954) and oxamide (Ayerst & Duke, 1954) have also been published.

Experimental

Unit cell and space group

Crystals of succinamide grown from water solutions were monoclinic plates bounded by {001} faces and showing perfect cleavage along {100}. Unit-cell dimensions were derived from single-crystal rotation photographs obtained with a Straumanis-type camera; they are, with their limits of error,

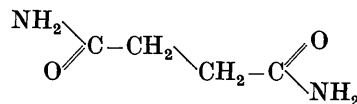
$$a_0 = 6.932 \pm 0.003, \quad b = 7.994 \pm 0.003, \quad c = 9.878 \pm 0.004 \text{ \AA}, \\ \beta = 102^\circ 28' \pm 5'.$$

The density observed by flotation is 1.442 ± 0.005 g.cm.⁻³, and the number of molecules per unit cell is 4 (calculated 3.998).

The observed systematic absences are hkl when $h+k$ is odd and $h0l$ when h or l are odd; they are characteristic of the space groups Cc (4 general positions) and $C2/c$ (centrosymmetric, 8 general positions).

Trial structure

A trial structure for succinamide



has been reported previously (Pasternak, 1953). The observations of (a) perfect cleavage of the crystals along {100}, (b) outstandingly strong ($h00$) reflections showing normal decline, (c) extremely weak ($hk0$) reflections when h and k are odd, (d) a very similar intensity distribution on layer lines with h even and with h odd, respectively, pointed to an almost perfect layer structure parallel to (100) with the layers of molecules at $x = \frac{1}{2}$ and $\frac{3}{2}$. By taking into account known bond lengths and bond angles, van der Waals distances, and the expectation of hydrogen bond formation, the configuration of the molecules and their

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arrangement within a layer was easily derived. The arrangement was consistent with the space group $C2/c$ with four centrosymmetric molecules in the unit cell.

Intensity data

Because of the shortness of the a axis and the apparent arrangement of the molecules in layers parallel to (100), Weissenberg photographs around a were most desirable. The crystals, however, were plates along (001) and could not be shaped into cylinders, as they cleaved almost on touch. An attempt was therefore made to modify the crystal habit by the addition of methylene blue to a hot concentrated aqueous solution of succinamide. This method proved to be successful; small laths or needles with a as the needle axis were obtained. A comparison between Weissenberg photographs taken with the modified and unmodified crystals showed no detectable differences in intensities, and a needle was therefore used for the intensity work; the specimen chosen had an almost square cross-section of about 0.2 mm. on edge. Equi-inclination Weissenberg photographs of the zero through fifth layer lines in respect to h were taken with Cu $K\alpha$ radiation, and of the zero through eighth layer lines with Mo $K\alpha$ radiation; the eighth layer line was very weak. In addition, the ($h0l$), ($h1l$), and ($h2l$) reflections were recorded with Cu radiation from a crystal oscillating around the b axis; they were used for the determination of an average anisotropic temperature factor along a (see below).

Intensities were estimated visually from multiple films, the range of intensities being 1 to 10,000. They were corrected in the usual way for Lorentz and polarization factors; no absorption or extinction corrections were applied. Factors correlating Cu to Mo data were derived by comparing the corrected intensities of a number of medium strong reflections common to both. Since the quality of the intensity data obtained from Cu radiation was considered superior to that obtained from Mo radiation, the Mo data were used only for those reflections lying outside the Cu sphere. A few reflections with noticeable intensities appeared even at spacings smaller than 0.5 Å, but this value was taken as limit of observation.

The data were brought to an absolute scale at a later stage by comparing, separately for each layer, the observed and calculated structure factors. The introduction of these additional parameters, the scale factors, was considered legitimate in view of the great number—about 1100—of observed structure factors.

The refinement of the structure

On the basis of the y and z parameters of the trial structure, and taking $x = \frac{1}{4}$ for all atoms, structure factors were calculated for all ($0kl$) and ($1kl$) reflections lying within the sphere of reflection for Cu radiation; no temperature factor was applied at this

stage. The agreement between calculated and observed structure factors was encouraging, the discrepancy factor R being 0.27.

The refinement of the y and z parameters progressed rapidly by the use of Fourier and difference Fourier projections and by least-squares treatment of the combined ($0kl$) and ($1kl$) data. When the reliability factor had been reduced to 0.17, after the contribution of the hydrogen atoms to the scattering of the structure and a temperature factor of $B = 0.85 \text{ \AA}^2$ had been introduced, three-dimensional refinement of the structure was begun. Structure factors for all reflections of the zero through fifth layer lines with $\sin \theta_{Mo}$ smaller than 0.6 were calculated, disregarding the obviously large temperature anisotropy along a , but the approximate scale factors which were obtained for each layer individually included a temperature-factor contribution. Three least-squares refinements of all the positional parameters were carried out; in addition to shifts in y and z , small, but significant, displacements of the atoms from the plane $x = \frac{1}{4}$ were obtained.

Although R had dropped to below 0.15, systematic discrepancies were apparent; in general, the (hkl), structure factors calculated stronger and the ($h\bar{k}l$) structure factors weaker than the observed ones. These discrepancies clearly originated from a large temperature anisotropy along a . The anisotropy had been taken into account only in a crude way, namely, as a constant for each layer line; this is not quite correct for a monoclinic crystal. For a monoclinic space group with an average anisotropic temperature factor T the structure factor has the form $F_c = F_g T$, where

$$T = \exp \left[-\frac{1}{4}(\alpha a^* h^2 + \beta b^* k^2 + \gamma c^* l^2 + \delta a^* c^* hl) \right]. \quad (1)$$

Here, F_g is the geometric part of the structure factor, α , β and γ are the average anisotropic temperature-factor coefficients along the reciprocal axes, and δ is a coefficient related to the orientation of the ellipsoid of anisotropy with respect to a^* and c^* . These coefficients are given in the same units as the isotropic temperature factor B . For symmetry reasons one axis of the ellipsoid must coincide with b^* .

The temperature factors of a pair of reflections the indexes of which differ only by the sign of l are not identical, because of the term $\exp[-\frac{1}{4}\delta a^* c^* hl]$. However, by taking ratios one obtains the simple relation

$$\frac{F(hkl)_o}{F(h\bar{k}l)_o} \approx \frac{F(hkl)_c}{F(h\bar{k}l)_c} = \frac{F(hkl)_g}{F(h\bar{k}l)_g} \exp \left[-\frac{1}{2}\delta a^* c^* hl \right], \quad (2)$$

which contains δ as single variable, assuming that the positional parameters have converged and that δ is independent of the scale factor. This expression is therefore very convenient for the determination of δ by least-squares methods. Such a least-squares calculation was carried out for the layer lines $h = 1$ to $h = 6$ individually and gave an average value of

$\delta = 2.1$, the average deviations of the individual values from the mean being 8%.

In the present structure the coefficient α can be obtained directly from δ by making the reasonable assumption that one principal axis of temperature anisotropy is perpendicular to the molecular layer, i.e. along a^* ; the other axes of anisotropy are then parallel to b^* and c . On transforming the temperature-factor expression (1) to orthogonal axes parallel to these principal axes of temperature anisotropy, the temperature factor becomes (see also Rollett & Davies, 1955)

$$T = \exp \left[-\frac{1}{4} \left\{ \alpha' a^{*2} (h + (c^*/a^*) \cos \beta^* l)^2 + \beta' b^{*2} k^2 + \gamma' \frac{c^{*2}}{\sin^2 \beta^*} l^2 \right\} \right]. \quad (3)$$

By comparing equations (1) and (3) the relationships between the coefficients $\alpha, \beta, \gamma, \delta$ and α', β', γ' , respectively, are easily derived; thus,

$$\alpha = \alpha', \quad \beta = \beta', \quad \gamma = \frac{\gamma'}{\sin^2 \beta^*} + \alpha' \cos^2 \beta^*, \quad \delta = 2 \cos \beta^* \alpha'.$$

Inserting the known values of δ and β^* into the last equation, the value $\alpha' = 4.9$ was obtained. A direct determination of α from the $(hk0)$, $(hk1)$, and $(hk2)$ data, taking β equal to γ and identical with the average in-plane temperature factor $B = 0.85 \text{ \AA}^2$, produced very nearly the same value, $\alpha' = 5.2$; it confirmed the assumption that the main axis of temperature anisotropy is perpendicular to the layer of the molecule.

All structure factors were now recalculated using the complete temperature-factor expression, and the scale factors were redetermined; the agreement between observed and calculated structure factors improved significantly. A three-dimensional difference Fourier, in which the contribution of hydrogen atoms to the calculated F 's was omitted, was then calculated in order to determine the individual atomic anisotropic temperature factors and to locate experimentally the hydrogen atoms. Peaks of heights approximately 1 e. \AA^{-3} were indeed found near the positions where hydrogen atoms were expected, namely, two in the plane of the molecule at a distance of 0.9 \AA from the nitrogen atom and two symmetrically above and below the plane at a distance of 1.0 \AA from carbon atom C_1 .

Sizeable differences in the magnitudes of the temperature anisotropies for the various atoms were apparent on the difference map; fortunately, however, the directions of the axes of the ellipsoid of anisotropy were for all atoms approximately parallel to a^* , b^* and c . The temperature factor for each atom was therefore represented by equation (3), α', β' and γ' being now the individual atomic temperature-factor coefficients. The magnitudes of these coefficients were determined by least-squares treatment of the complete data. Three refinements similar to those described by

Davies & Blum (1955) were carried out, interspersed with adjustment of the scale factors of the layer lines. In a final step, the positional parameters were also adjusted by least squares. The shifts in the parameters were barely significant, the maximum being 0.004 \AA .

It is interesting to note that in the refinement of the structure of succinamide the large atomic temperature anisotropies virtually did not interfere with the determination of the positional parameters. This may be due to a special feature of the structure; namely, that the large temperature vibration is along a direction in which atoms are very widely spaced, and therefore there is little interaction between vibrational and positional parameters.

The final positional and vibrational parameters of the atoms are listed in Table 1. The average standard

Table 1. *Atomic coordinates*

	x	y	z	$\alpha' (\text{\AA}^2)$	$\beta' (\text{\AA}^2)$	$\gamma' (\text{\AA}^2)$
C_1	0.2496	-0.1943	0.0611	4.50	0.95	1.28
C_2	0.2537	-0.0097	0.0285	3.85	0.82	1.22
N	0.2532	0.0933	0.1346	5.86	1.04	1.30
O	0.2559	0.0429	-0.0890	6.37	1.01	1.10
H_1	0.125	-0.225	0.110			
H_2	0.375	-0.225	0.110			
H_3	0.250	0.203	0.117			
H_4	0.250	0.055	0.220			

error in the positional parameters was calculated as $2.2 \times 10^{-3} \text{ \AA}$ in x and $1.4 \times 10^{-3} \text{ \AA}$ in y and z ; the standard error in the bond lengths is then $2 \times 10^{-3} \text{ \AA}$ except for the C_1-C_1 bond, its standard error being larger ($3 \times 10^{-3} \text{ \AA}$) because the two carbon atoms are related by a center of symmetry. The standard error in the bond angles is $10'$.

The final structure-factor agreement is very satisfactory. In Table 2 the observed and calculated ($Ok1$) and ($1kl$) structure factors are compared.* The discrepancy factors are given in Table 3 as a function of h ; they are virtually independent of h . The over-all R factor is 0.089. Structure factors too weak to be observed were omitted; with very few exceptions they calculated weaker than the minimum observable values. The few very strong reflections show pronounced extinction and are also omitted in the calculation of the R factor.

As a final check of the results a Fourier section and a difference Fourier section at $x = \frac{1}{4}$ were calculated. The Fourier section (Fig. 1(a)) is remarkable for the resolution and the heights of the electron density peaks, their heights being about 14, 16 and 18 e. \AA^{-3} for the carbon, nitrogen and oxygen atoms, respec-

* A list of about 1100 values of F_o and F_c has been deposited as Document No. 4719 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting \$2.50 for photoprints, or \$1.75 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table 2. Observed and calculated structure factors

The calculations are based on McWeeny scattering curves (1951). The F 's are multiplied by ten.

k	l	F _o	F _c	k	l	F _o	F _c	k	l	F _o	F _c	k	l	F _o	F _c
		Ok		10	2	84	74	5	13	46	43	3	3	297	290
				10	3	60	57	5	14	34	8	3	4	235	226
				10	4	29	25	5	15	35	4	3	5	343	351
				10	5	29	25	5	16	36	24	3	6	143	124
	2	573	839	10	6	80	77	7	7	14	1	3	7	30	31
	4	441	464	10	7	31	55	7	8	53	64	3	8	196	204
	6	253	266	10	8	32	13	7	9	64	64	3	9	30	17
	8	103	103	10	9	40	13	7	10	64	43	10	10	162	172
10		447	522	10	10	40	13	7	11	64	11	11	11	224	21
12		336	311	10	11	35	13	7	12	51	48	12	12	92	103
14		206	200	10	12	33	20	7	13	59	66	13	13	48	45
16		54	60	10	13	36	29	7	14	57	74	14	14	39	33
18		7	0	10	14	36	29	7	15	57	86	15	15	33	54
				12	2	22	4	7	16	57	86	16	16	33	6
				12	1	22	13	7	17	57	86	17	17	33	6
				12	2	22	13	7	18	57	86	18	18	33	6
				12	3	22	13	7	19	57	86	19	19	33	6
				12	4	22	13	7	20	57	86	20	20	33	6
				12	5	22	13	7	21	57	86	21	21	33	6
				12	6	22	13	7	22	57	86	22	22	33	6
				12	7	22	13	7	23	57	86	23	23	33	6
				12	8	22	13	7	24	57	86	24	24	33	6
				12	9	22	13	7	25	57	86	25	25	33	6
				12	10	22	13	7	26	57	86	26	26	33	6
				12	11	22	13	7	27	57	86	27	27	33	6
				12	12	22	13	7	28	57	86	28	28	33	6
				14		35	36	9		11	1				
				14	1	66	64	9	1	22	146	10	1	22	29
				14	2	66	64	9	2	33	64	11	2	33	74
				14	3	75	80	9	3	44	94	11	3	44	26
				14	4	67	66	9	4	55	76	11	4	55	52
				14	5	44	44	9	5	66	10	11	5	66	13
				14	6	44	44	9	6	77	162	11	6	77	2
				14	7	45	44	9	7	88	21	11	7	88	29
				14	8	45	44	9	8	99	51	11	8	99	75
				14	9	45	44	9	9	110	39	11	9	110	62
				14	10	45	44	9	10	121	28	11	10	121	9
				14	11	45	44	9	11	132	28	11	11	132	9
				14	12	45	44	9	12	143	28	11	12	143	9
				14	13	45	44	9	13	154	37	11	13	154	44
				14	14	45	44	9	14	165	32	11	14	165	77
				14	15	45	44	9	15	176	26	11	15	176	80
				14	16	45	44	9	16	187	25	11	16	187	96
				11		47	38	11		30	78	11		30	43
				11	1	75	82	11	1	41	189	11	1	41	72
				11	2	157	166	11	2	52	69	11	2	52	115
				11	3	275	289	11	3	63	118	11	3	63	84
				11	4	125	133	11	4	74	24	11	4	74	69
				11	5	87	64	11	5	85	17	11	5	85	17
				11	6	77	74	11	6	96	17	11	6	96	17
				11	7	130	136	11	7	107	28	11	7	107	37
				11	8	251	284	11	8	118	40	11	8	118	69
				11	9	97	101	11	9	129	28	11	9	129	3
				11	10	157	183	11	10	140	17	11	10	140	43
				11	11	200	15	11	11	151	40	11	11	151	153
				11	12	199	29	11	12	162	2	11	12	162	48
				11	13	31	1	11	13	173	16	11	13	173	97
				11	14	60	59	11	14	184	37	11	14	184	85
				11	15	34	14	11	15	195	71	11	15	195	1
				11	16	35	12	11	16	206	12	11	16	206	18
				11	17	36	36	11	17	217	1	11	17	217	59
				15		44	17	15		33	1	15		33	49
				15	1	99	57	15	1	44	28	15	1	44	73
				15	2	239	378	15	2	55	266	15	2	55	39
				15	3	339	441	15	3	66	37	15	3	66	46
				15	4	444	511	15	4	77	78	15	4	77	42
				15	5	555	588	15	5	88	6	15	5	88	1
				17		93	96	17		109	96	17		109	32
				11		80	78	11		120	78	11		120	78
				11	1	181	198	11	1	131	75	11	1	131	75
				11	2	321	340	11	2	142	121	11	2	142	121
				11	3	461	480	11	3	153	181	11	3	153	181
				11	4	601	640	11	4	164	241	11	4	164	241
				11	5	741	780	11	5	175	301	11	5	175	301
				11	6	881	920	11	6	186	361	11	6	186	361
				11	7	1021	1060	11	7	197	421	11	7	197	421
				11	8	1161	1200	11	8	208	481	11	8	208	481
				11	9	1301	1340	11	9	219	541	11	9	219	541
				13		111	1	13		122	349	13		122	14
				13	1	222	233	13	1	133	394	13	1	133	394
				13	2	333	344	13	2	144	439	13	2	144	439
				13	3	444	455	13	3	155	484	13	3	155	484
				13	4	555	566	13	4	166	529	13	4	166	529
				15		111	1	15		122	84	15		122	27
				15	1	222	233	15	1	133	99	15	1	133	99
				15	2	333	344	15	2	144	114	15	2	144	114
				15	3	444	455	15	3	155	129	15	3	155	129
				15	4	555	566	15	4	166	144	15	4	166	144
				15	5	666	677	15	5	177	159	15	5	177	159
				15	6	777	788	15	6	188	174	15	6	188	174
				15	7	888	899	15	7	199	189	15	7	199	189
				15	8	999	999	15	8	200	204	15	8	200	204
				15	9	1000	1000	15	9	201	219	15	9	201	219
				15	10	1111	1111	15	10	202	234	15	10	202	234
				15	11	1222	1222	15	11	203	249	15	11	203	249
				15	12	1333	1333	15	12	204	264	15	12	204	264
				15	13	1444	1444	15	13	205	279	15	13	205	279
				15	14	1555	1555	15	14	206	294	15	14	206	294
				15	15	1666	1666	15	15	207	309	15	15	207	309
				15	16	1777	1777	15	16	208	324	15	16	208	324
				15	17	1888	1888	15	17	209	339	15	17	209	339
				15	18	1999	1999	15	18	210	354	15	18	210	354
				15	19	2000	2000	15	19	211	369	15	19	211	369
				15	20	2111	2111	15	20	212	384	15	20	212	384
				15	21	2222	2222	15	21	213	399	15	21	213	399
				15	22	2333	2333	15	22	214	414	15	22	214	414
				15	23	2444	2444	15	23	215	429	15	23	215	429
				15	24	2555	2555	15	24	216	444	15	24	216	444
				15	25	2666	2666	15	25	217	459	15	25	217	459
				15	26	2777	2777	15	26	218	474	15	26	218	474
				15	27	2888	2888	15	27	219	489	15	27	219	489
				15	28	2999	2999	15	28	220	504	15	28	220	504
				15	29	3000	3000	15	29	221	519	15			

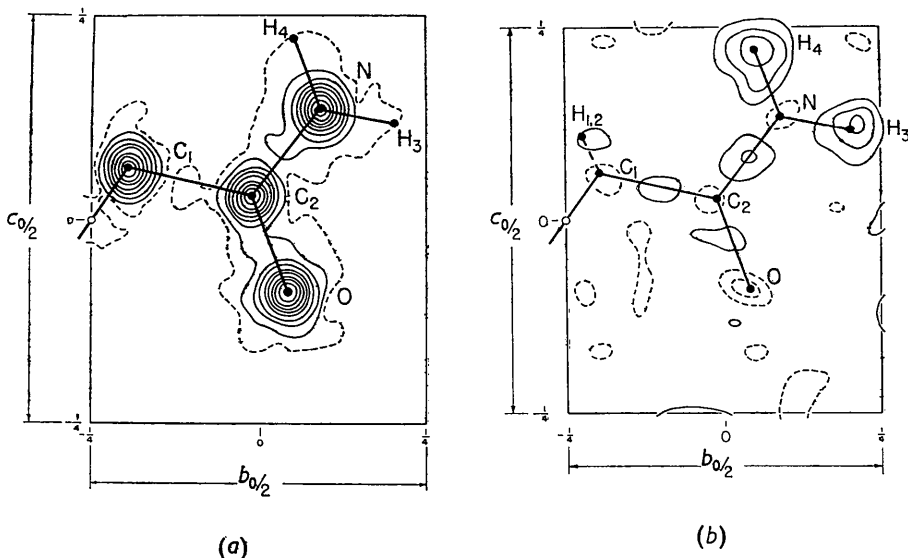


Fig. 1. (a) Fourier section at $x = \frac{1}{4}$. Broken contour at $1 \text{ e.}\text{\AA}^{-3}$, other contours at 2, 4, 6, ... $\text{e.}\text{\AA}^{-3}$. (b) Difference Fourier section at $x = \frac{1}{4}$. Contours at 0.25, 0.5, 0.75... $\text{e.}\text{\AA}^{-3}$. Negative contours are broken.

Fourier section (Fig. 1(b)). The general background of the difference Fourier is very low, almost everywhere less than $\pm 0.25 \text{ e.}\text{\AA}^{-3}$. The hydrogen atoms, which are attached to the nitrogen atom, appear as well-defined, fairly round peaks of heights about $1 \text{ e.}\text{\AA}^{-3}$; the N-H bonds are very probably coplanar with the molecule and form angles of about 120° with the C-N bond. Hydrogen atoms H_1 and H_2 , which are 0.8 \AA above and below the plane, also seem to show up weakly. All the heavy atoms fall into holes, the oxygen atom into a fairly deep one. By contrast, a positive electron density is found between bonded atoms, especially between C_2 and N. As for the physical meaning of this observed electron-density variation, it is difficult to escape the conclusion that a partial displacement of electrons from the atoms into the bonds is being observed. However, it should be pointed out that all refinements were carried out by least-squares methods, and the weights given to individual reflections were different from those in the difference Fourier synthesis; refinement of the temperature factors based on the difference Fourier and, in addition, introduction of the anisotropic f curve for the oxygen atom (McWeeny,

1951) might have smoothed the difference Fourier somewhat.

It is felt that the refinement has approached the limit set by the errors in the intensity measurements; more convincing evidence for the displacement of the electrons would have to be based on more accurate experimental data.

Discussion of the structure

Molecular configuration

One layer of the structure of succinamide is shown in Fig. 2; bond lengths and angles are also listed in Table 4.

Table 4. Bond lengths and angles

C_1-C_1	1.501 \AA	$C_1-C_1-C_2$	$113^\circ 54'$
C_1-C_2	1.512	C_1-C_2-N	$115^\circ 36'$
C_2-N	1.333	C_1-C_2-O	$122^\circ 23'$
C_2-O	1.238	$N-C_2-O$	$122^\circ 2'$
$N \cdots O$	$\left\{ \begin{array}{l} 2.942 \\ 2.939 \end{array} \right.$	$C_2-N \cdots O$	$\left\{ \begin{array}{l} 119^\circ 23' \\ 120^\circ 5' \end{array} \right.$

A comparison of the molecular configuration of succinamide with those of succinic acid (Morrison & Robertson, 1949) and oxamide (Ayerst & Duke, 1954) is most fruitful. Both of these structures, and especially the latter, have been determined with great care.

The succinamide molecule is perfectly planar; no atom deviates from the median plane by more than the standard error associated with it. This contrasts with the configuration of succinic acid, in which the planes of the carboxyl groups are rotated by 9° in respect to the plane of the carbon chain, the four carbon atoms being coplanar. However, perfect planarity was observed for the molecule of oxamide.

Table 3. Discrepancy factor R as a function of h

h	Number of observed reflections	R
0	89	0.082
1	141	0.084
2	165	0.085
3	154	0.092
4	128	0.087
5	135	0.090
6	101	0.099
7	96	0.115
8	69	0.096
hkl	1078	0.089

Of the two non-equivalent C-C bonds the central C_1-C_1 bond is slightly, but significantly, shorter (1.501 Å compared to 1.512 Å); both bonds are shorter than the value of 1.54 Å usually assigned to

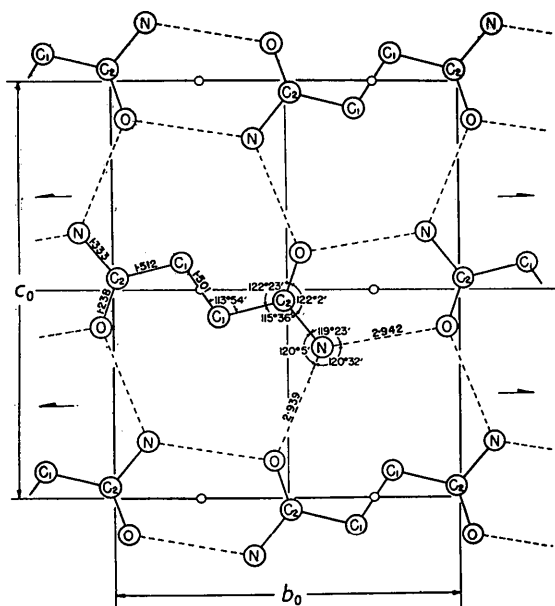


Fig. 2. A schematic drawing showing the arrangement of the molecules in the layer $x = \frac{1}{4}$.

a C-C single bond. Furthermore, the $C_1-C_1-C_2$ bond angle ($113^\circ 54'$) is appreciably larger than the tetrahedral angle. These observations are in accord with the tentative results of Morrison & Robertson (1949) in their studies of succinic acid and other dicarboxylic acids containing an even number of carbon atoms. In particular, they report an alternation between long and short C-C bonds along the chain, the bond adjacent to the carboxyl group always being the longer. This systematic variation in the bond lengths might be explained by hyperconjugation.

In the amide group of succinamide the C-O bond has the same length as in oxamide, but the C-N bond

Table 5. Bond lengths in the amide group

	C-O (Å)	C-N (Å)	Reported standard error (Å)
Acetamide	1.28	1.38	?
Succinamide	1.238	1.333	0.002
Oxamide	1.243	1.315	0.004
Formamide	1.225	1.30	0.017
Glycyl asparagine*	1.22	1.36	0.014
Glutamine	1.27	1.28	0.024
Peptide (average)†	1.24	1.32	—

* A value of 1.39 Å for the C-N bond had been reported in the original paper (Pasternak *et al.*, 1954). On checking the calculations, an error in the x coordinate of nitrogen atom N_1 has been discovered (correct $x = -0.064$); the corrected bond length is reported here. Other molecular dimensions involving this atom do not change significantly.

† Corey & Pauling, 1953.

is somewhat longer (1.333 Å compared with 1.315 Å). It is interesting to note that, except for this small though significant difference, the lengths of the C-O and of the C-N bonds in the amide groups of all terminal amides and peptides studied to date have been found to be the same within the limits of error of the investigations (Table 5).

The amide group of succinamide, however, differs pronouncedly from other amides in the relative values of the three bond angles around the carbon atom (Table 6). In succinamide angle O-C-C is slightly

Table 6. Bond angles in the amide group

	N-C-C (°)	O-C-C (°)	O-C-N (°)
Acetamide	109	129	122
Succinamide	115.6	122.4	122.0
Oxamide	114.8	119.5	125.7
Glycyl asparagine*	115.2	124.9	119.9
Glutamine*	118	118	123
Peptide (average)†	114	121	125

* In terminal amide.

† Corey & Pauling, 1953.

larger than angle O-C-N, but in oxamide and in peptide amide links the former angle is significantly smaller than the latter. The variation in bond angles as found in peptide amide links agrees with what one might expect on the basis of resonance considerations. It is interesting, however, that in succinamide, and even more pronouncedly in the terminal amide group of its derivative glycylasparagine, the angles deviate from the predicted ones. Similar deviations in the relative magnitudes of the angles were reported also for the carboxyl groups of *N*-acetylglycine (Carpenter & Donohue, 1950), succinic acid, and glutaric acid (Morrison & Robertson, 1949).

Finally, the three bonds formed by the nitrogen atom in succinamide are coplanar and trigonally arranged within the accuracy of the determination of the hydrogen atoms.

Arrangement of the molecules

The plane of the succinamide molecules is slightly but significantly tilted in respect to the (100) plane; the two planes intersect approximately along the C_1-C_1 bond, and the dihedral angle between them is 1.0° . The molecules in the layer are connected by a net of hydrogen bonds. There are two sets of non-equivalent hydrogen bonds, which have, however, the same length and form angles of very nearly 120° with the C-N bond. The hydrogen bonds are arranged not quite so symmetrically around the oxygen atoms, the angles being $118^\circ 35'$ and $138^\circ 31'$. One set of hydrogen bonds joins the amide groups of adjacent molecules into an eight-membered ring around a center of symmetry. The same ring formation is found in oxamide, which displays a very similar arrangement of the molecules in the layer, and in formamide (Ladell & Post, 1954). It is interesting that these hydrogen

bonds, which are of identical length in the three structures, are fairly long, 2.94 Å.

The spacing between molecular layers is 3.385 Å, compared with 3.007 Å in oxamide. The increase in spacing is reasonable considering the presence of the bulky methylene groups in succinamide; in both structures, however, the packing is very loose, assuming conventional van der Waals radii for the individual atoms.

The superposition of two molecular layers in the unit cell is shown in Fig. 3. In this view along a , the

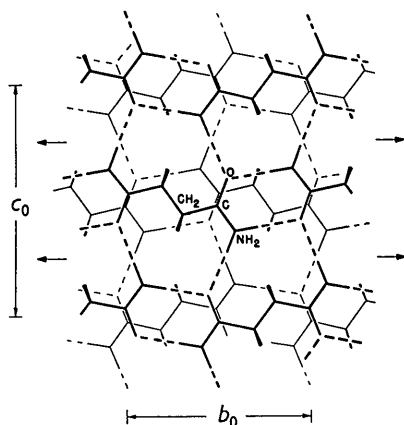


Fig. 3. A schematic drawing of the structure viewed along the a axis of the crystal. The molecular layers are at $x = \frac{1}{4}$ and $x = \frac{3}{4}$, and the twofold axes are at $x = 0, \frac{1}{2}$.

structure might be described as consisting of sheets of molecules parallel to the (001) plane; these sheets are held together by hydrogen bonds.

Finally, the anisotropic temperature factors of the structure (Table 1) are well explained by the packing of the molecules. The largest temperature vibrations are, as expected, perpendicular to the molecular layers. The oxygen and nitrogen atoms, which form only one covalent bond (not counting those with hydrogen atoms), have the largest temperature factors, and carbon atom C_2 , which forms three bonds, has the smallest. Within the layer the temperature factors are small, vibrations along c being somewhat larger than along b .

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