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The Crystal Structures of the Dimorphs of DL-Methionine

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DL-Methionine (DL-2-amino-4-methyl-thiobutanoic acid) crystallises in two monoclinic forms. The dimorph with space group $P2_1/a$ is termed the α-form, that with space group $I2/a$, the β-form. The crystal structures have been analysed from single-crystal diffraction data using copper radiation. The intra-molecular and hydrogen-bond lengths in the two forms are similar. The structures of both are based on the stacking of double-layer units along the c axis, the individual double layer being rigidly bound by hydrogen bonds. Adjacent layers are held by van der Waals forces acting between the terminal methyl–sulphur groups. Rotation of the terminal carbon–sulphur bond permits two balanced arrangements of these van der Waals bonds corresponding to the dimorphs of methionine.

Introduction

As part of the work of this laboratory on the structure of proteins, the analyses of the crystal structures of certain α-amino acids are being undertaken. From these studies, the detailed configuration of the R groups in polypeptide chains can be derived. Consideration of the α-amino acids in groups of similar chemical structure leads to a reduction in the effort necessary to elucidate their crystal structures since the analysis of one member of the group is an aid in the solution of the remaining members. A previous communication (Dawson & Mathieson, 1951) has indicated the relationship of the packing arrangements of the straight- and branched-chain aliphatic α-amino acids. Since methionine is the only member containing an atom of relatively high atomic number (sulphur= 16), it was decided to analyse this compound first as a representative of the straight-chain aliphatic α-amino acids.

Some crystallographic measurements have been made by Albrecht, Schnakenberg, Dunn & McCullough (1943) but it is difficult to reconcile their results with those of the present study. They have therefore been assumed in error.

The occurrence of dimorphism in DL-methionine has not been recorded previously and adds greatly to the interest of the final results.

Experimental

Crystals of DL-methionine, grown from an ethyl alcohol–water solution by slow evaporation, occur as soft plates, the main face being (001). In attempting to grow crystals of greater plate thickness from several crystallization batches, it was found that there were two crystalline forms, both monoclinic. The two forms were differentiated by means of diffraction photographs of the {010} zone. They appear to be of almost equal stability.

The cell dimensions were determined from rotation photographs and the space-group data from zero- and n-layer photographs taken on an equi-inclination Weissenberg goniometer (Mathieson, 1951). The densities were measured by flotation in a benzene–chloroform mixture. The relevant data from the two forms, as given in the previous paper, are:

	α-Methionine	β-Methionine
a (Å)	9·76	9·94
b (Å)	4·70	4·70
c (Å)	16·70	33·40
β (°)	102	106·6
$d_{\text{meas.}}$	1·34	1·34
$d_{\text{calc.}}$	1·33	1·33
Z	4	8
Space group	$P2_1/a$	$I2/a$

For α-methionine, (hkl) intensity data were derived from zero- and n-layer equi-inclination films. The layer-line exposures were made proportional to $\cos^2\mu$, and the Lp^{-1} correction factors were applied by the use of charts (Kaan & Cole, 1950). For β-methionine, intensity measurements were made only on the {010} and {100} zones of reflexions. The multiple-film technique with visual estimation of the intensities was used. Because the crystals are plate-like, and slightly distorted owing to their softness, the reflexions are of a variable shape and the accuracy of intensity measurement cannot be considered as high as normally achieved with this method. An attempt was made to provide partial correction by taking into account the spread of each reflexion.

The observed structure amplitudes were placed on an absolute basis by scaling against the calculated values. For the calculation of structure amplitudes, scattering curves for S, C, N and O from *Internationale Tabellen* were corrected by a temperature factor obtained by plotting $\Sigma(F_c/F_o)$ against $2\sin\theta$ in ranges $\sin^2\theta = 0{\cdot}0$–$0{\cdot}2$, $0{\cdot}2$–$0{\cdot}4$, ..., $0{\cdot}8$–1. The final temperature factor was $B = 3{\cdot}1\times10^{-16}$ cm.^{2}.

All Fourier summations were carried out by means of three-figure Beevers–Lipson strips at 6° intervals with the exception of the c axis of β-methionine which was subdivided into 120 parts. The electron-density and vector maps were drawn from contour values derived from interpolated sections.

Determination of the crystal structure of α-methionine

The presence of the moderately heavy sulphur atom in methionine allows the structure analysis to proceed in a direct manner by the use of Patterson–Harker sections. The $F^2(hkl)$ values were combined to give the sections of the three-dimensional Patterson vector distribution at $y = \frac{1}{2}$ and 0 by equations (i) and (ii) respectively:

$$P(u, \tfrac{1}{2}, w) = \sum_h \sum_l \left[\sum_k (-1)^k F^2(hkl)\right] \times \cos 2\pi \left(\frac{hx}{a} + \frac{lz}{c}\right), \tag{i}$$

$$P(u, 0, w) = \sum_h \sum_l \left[\sum_k F^2(hkl)\right] \times \cos 2\pi \left(\frac{hx}{a} + \frac{lz}{c}\right). \tag{ii}$$

The resulting contour maps are shown in Figs. 1 and 2. To discuss the elucidation of the vector maps, it is convenient to designate the four molecules of methionine in the unit cell as in Fig. 4. A and B (also C and D) are related by the glide plane parallel to a, whereas A and C (also B and D) are related by the screw axis parallel to b at $x = \pm\frac{1}{4}$, $z = 0$. The individual atoms can thus be designated by subscripts indicative of the molecule, e.g. C_{3B}. In the Patterson section $P(u, \frac{1}{2}, w)$, vectors occur due to pairs of atoms which are related by a diad screw axis or fortuitously placed so that they have a vector component of approximately $\frac{1}{2}b$. The principal peak is P and is due to the vector S_A–S_C (and S_B–S_D). It is notable that another large peak, Q, occurs at $x = \frac{1}{2}$, $z = 0$. If this vector arises from sulphur atoms related by the glide plane parallel to a, then these atoms must lie at approximately $\frac{1}{4}b$ from this glide plane and their y parameters are approximately 0 and $\frac{1}{2}b$. This is confirmed in the section $P(u, 0, w)$ (Fig. 2) by the appearance of the peak R which arises from vector S_C–S_B (and S_A–S_D). The atoms S_C and S_B are both near the level $y = \frac{1}{2}b$ and are related by a centre of symmetry. Atoms S_A and S_D are near the level $y = 0$ and are similarly related. Thus the parameters of the sulphur atom of the asymmetric unit (molecule) are fixed, x and z accurately and y approximately. It is then necessary to locate the remaining atoms in the molecule. Should any of these atoms lie near the y level of S_A, then vectors with respect to S_C and S_B will appear in $P(u, \frac{1}{2}, w)$ and with respect to S_D in $P(u, 0, w)$. Since the height of a vector peak is dependent on vector multiplicity and the product of the atomic numbers of the component atoms, these vectors S–X will be of greater significance than any vector $X-X$ where X = C, N or O. Comparison of the vector distributions to the right of peaks P, Q and R in Figs. 1 and 2 show their remarkable similarity, indicating that this distribution does arise from the remainder of the molecule. By this means C_4, C_3, C_2, C_1, N and O_1 are located. The vector S–O_2 is not observed and the position of C_5 is somewhat dubious, but the marked appearance of the peak at U and not at V enables a decision to be made. The atom O_2 can be placed approximately on the basis of the known configuration of the carboxyl group. The disposition of the molecule in the projection was thus deduced directly. With this model, structure amplitudes

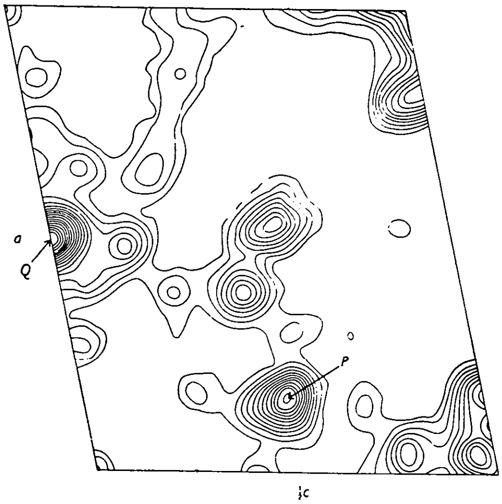

Fig. 1. Patterson–Harker section $P(u, \frac{1}{2}, w)$ for α-methionine. Scale: 1 cm. = 1·6 Å.

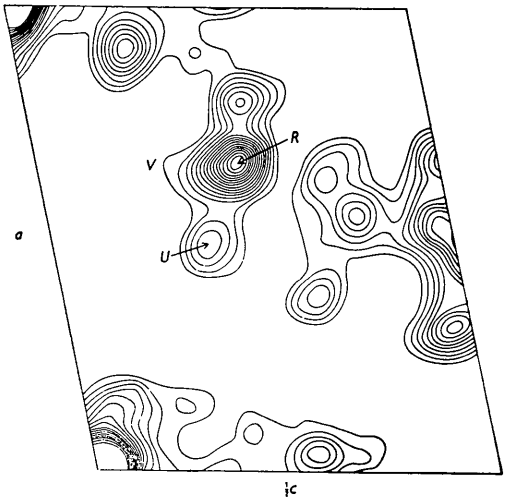

Fig. 2. Patterson–Harker section $P(u, 0, w)$ for α-methionine. Scale: 1 cm. = 1·6 Å.

for $h0l$ reflexions were calculated, the discrepancy being somewhat high (37%). However, the first Fourier contour map of the projection along the b axis was satisfactory, allowing atomic parameters to be more accurately determined and, with the additional signs fixed, the final electron-density map was obtained as shown in Fig. 3. The final discrepancy was 21%.

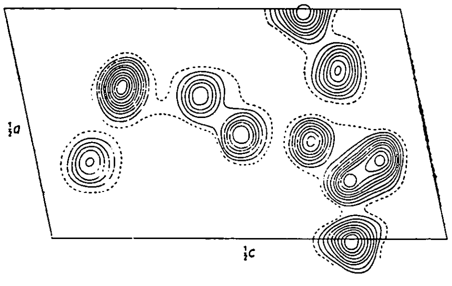

Fig. 3. Electron-density projection on (010) for α-methionine. Contours for the sulphur atom are drawn at intervals of 2 e.Å^{-2}, and for other atoms at 1 e.Å^{-2}. The 2 e.Å^{-2} contour is shown by broken lines. Scale: 1 cm. = 1·6 Å.

The crystal structure viewed down the b axis is shown in Fig. 4.

The y parameters were determined from the projection down the a axis. From the two Patterson–Harker sections, the relative y parameters of most atoms in the molecule with respect to the sulphur atom were estimated approximately, since the peak height of a vector in any section is related to its y component. Combining the accurate projected bond lengths and provisional normal bond lengths, these relative y parameters were refined to derive a more precise molecular model. This model had then to be moved parallel to the b axis, maintaining the sulphur atom near $y = 0$ until a reasonable set of calculated structure amplitudes was achieved. Refinement by several Fourier syntheses yielded the final electron-density map shown in Fig. 5, the discrepancy being 21%. The corresponding diagram of the crystal structure is given in Fig. 6.

The atomic coordinates are collected in Table 1, and the interatomic distances and bond angles calculated from these in Table 2. The lettering of the atoms in Table 2 relates to Fig. 11 (a). The use of this diagram avoids the necessity for obscuring detail of Fig. 4 and also shows more clearly the relationship of the molecule to its neighbours.

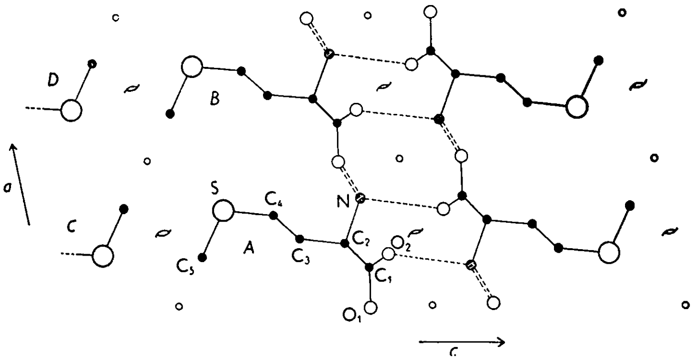

Fig. 4. The crystal structure of α-methionine projected down the b axis. Hydrogen bonds are shown by broken lines. Scale: 1 cm. = 2·5 Å.

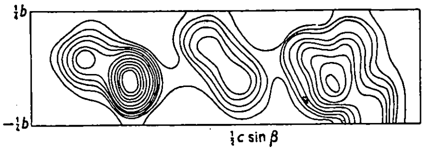

Fig. 5. Electron-density projection down the a axis for α-methionine. Contours for sulphur and for the group $C_2NC_1O_1O_2$ are drawn at intervals of 2 e.Å^{-2}. Scale: 1 cm. = 1·6 Å.

The details of the crystal structure of α-methionine will be discussed in conjunction with that of β-methionine. For the deduction of the structure of β-methionine, it is sufficient to note the position of

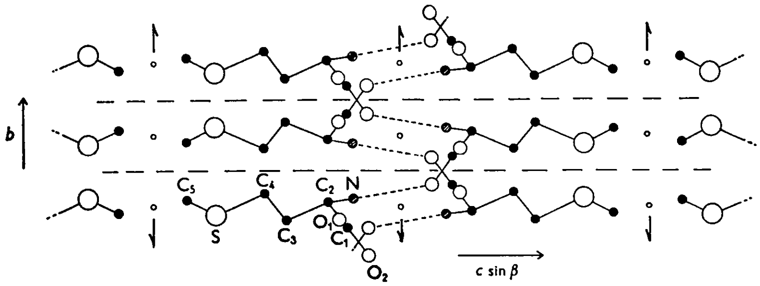

Fig. 6. The crystal structure of α-methionine projected down the a axis. Scale: 1 cm. = 2·5 Å.

the group $C_2NC_1O_1O_2$ and its associated hydrogen bonding to adjacent groups in relation to the screw axes and centres of symmetry at $z = \frac{1}{2}$ (Fig. 4).

Table 1. *Atomic co-ordinates as fractions of the corresponding cell edges for α-methionine*

	x	y	z
S	0·328	−0·056	0·128
O_1	0·007	−0·094	0·378
O_2	0·174	−0·342	0·435
N	0·364	0·053	0·406
C_1	0·125	−0·144	0·392
C_2	0·218	0·028	0·353
C_3	0·225	−0·096	0·268
C_4	0·311	0·093	0·224
C_5	0·164	0·047	0·068

Table 2. *Interatomic distances and bond angles in α-methionine*

C_5–S	1·77 Å	C_5–S –C_4	100°
S–C_4	1·79	S–C_4–C_3	111
C_4–C_3	1·51	C_4–C_3–C_2	111
C_3–C_2	1·55	C_3–C_2–C_1	111
C_2–C_1	1·47	C_2–C_1–O_1	120
C_2–N	1·52	C_2–C_1–O_2	119
C_1–O_1	1·28	O_1–C_1–O_2	121
C_1–O_2	1·21	C_3–C_2–N	110
		C_1–C_2–N	112
C_5–${}_1C_5$	3·55	${}_1O_1$–N–${}_2O_1$	117
C_5–${}_2C_5$	3·87	C_2–N–${}_1O_1$	111
C_5–${}_3C_5$	3·87	C_2–N–${}_2O_1$	105
S–${}_2C_5$	4·34	C_2–N–${}_1O_2$	106
S–${}_3C_5$	3·78	C_1–O_2–${}_1$N	126
N–${}_1O_1$	2·92	C_1–O_1–${}_2$N	125
N–${}_2O_1$	2·59	C_1–O_1–${}_3$N	109
N–${}_1O_2$	2·80		

Determination of the crystal structure of β-methionine

The cell dimensions of β-methionine are similar to those of α-methionine except for the doubling of the c axis (the cell being body-centred) and a small increase in the angle β. Whereas for α-methionine, with space group $P\,2_1/a$, diad screw axes repeat parallel to the c axis at distances of 8·35 Å, for β-methionine, with space group $I2/a$, screw axes alternate with diad rotation axes (cf. Figs. 4 and 9). It is probable that, on account of the equal stability of the two forms, the system of hydrogen bonding which basically determines the crystal structure of α-methionine will remain unchanged. Thus the roup $C_2NC_1O_1O_2$ of the asymmetric unit (which is the molecule) may be disposed around the screw axis at $x = 0$, $z = \frac{1}{4}$ with reasonable accuracy, taking into account the hydrogen bonding to adjacent units. To

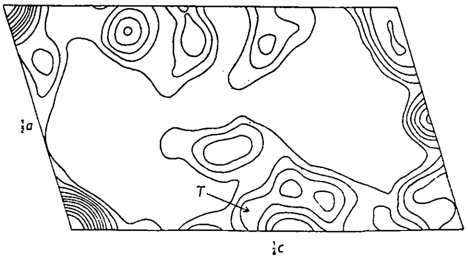

Fig. 7. Patterson projection down the b axis for β-methionine. Scale: 1 cm. = 1·6 Å.

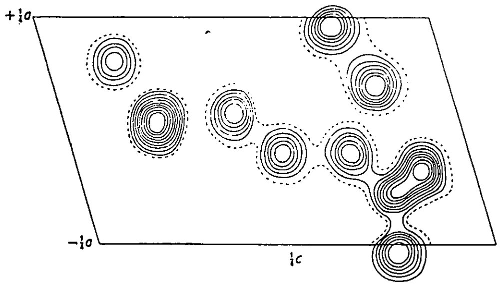

Fig. 8. Electron-density projected on (010) for β-methionine. Contours are as in Fig. 3. Scale: 1 cm. = 1·6 Å.

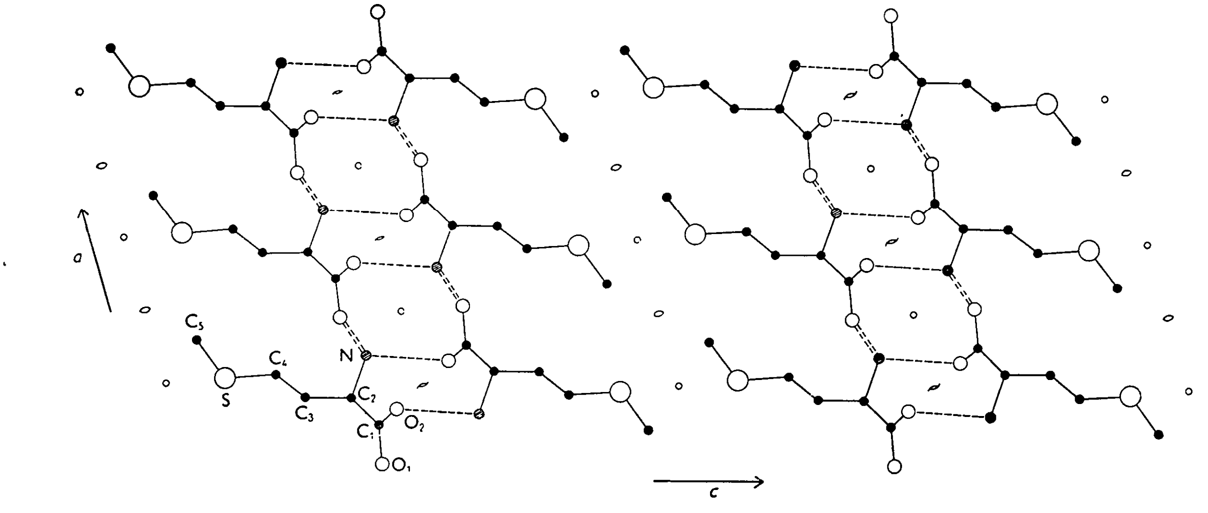

Fig. 9. The crystal structure of β-methionine projected on (010). Hydrogen bonds are shown by broken lines. Scale: 1 cm. = 2·5 Å.

locate the remainder of the molecule, a Patterson projection along the *b* axis (Fig. 7) was used. The S–S vector is not immediately evident since its 'weight' in such a projection is nearly equal to any S–*X* vector (X = C, N or O) because of the relative multiplicity. However, using the assumed disposition of the $C_2NC_1O_1O_2$ residue, the best fit is achieved when the peak *T* is ascribed to the S–S vector although its contour height is only 10 whereas there are several others ranging from 15 to 25. The increase in the β angle indicates that the C_5–S bond now lies in the plane of the carbon chain C_2–C_4. Combining this information, a model was obtained giving satisfactory agreement with observed structure amplitudes, and refinement was carried out by means of successive Fourier syntheses. The final parameters were derived from the electron-density contour map (Fig. 8) the discrepancy with observed structure amplitudes being 21%. The crystal structure viewed down this axis is shown in Fig. 9.

To determine the *y* parameters, the projection along the *a* axis was used. Fixing the approximate position of the molecule was relatively straightforward since it is known from the structure of α-methionine that the main part of the molecule will be located at approximately $\frac{1}{4}b$ from the glide plane (in this case passing through the origin of the cell). The atomic positions relative to the sulphur atom were assumed to be as in α-methionine and the model was then moved near the level $y = \frac{1}{4}b$ until a good fit with observed structure amplitudes was attained. The final discrepancy after several syntheses was 23%. The final electron-density map is not shown since it has close similarity to that of α-methionine (Fig. 6). The crystal structure viewed along the *a* axis is given in Fig. 10; the atomic parameters are collected in Table 3 and the inter-atomic distances and bond angles in Table 4. The approach distances of atoms in adjacent molecules are shown more clearly in Fig. 11(*b*).

Table 3. *Atomic co-ordinates as fractions of the corresponding cell edge for β-methionine*

	x	*y*	*z*
S	0·017	0·172	0·059
O_1	−0·270	0·192	0·187
O_2	−0·091	−0·078	0·216
N	0·099	0·306	0·203
C_1	−0·142	0·122	0·194
C_2	−0·049	0·306	0·175
C_3	−0·051	0·169	0·131
C_4	0·038	0·336	0·109
C_5	0·151	0·350	0·043

Table 4. *Interatomic distances and bond angles in β-methionine*

C_5–S	1·78 Å	C_5–S –C_4	100°
S–C_4	1·80	S–C_4–C_3	109
C_4–C_3	1·54	C_4–C_3–C_2	113
C_3–C_2	1·58	C_3–C_2–C_1	108
C_2–C_1	1·52	C_2–C_1–O_1	118
C_2–N	1·50	C_2–C_1–O_2	120
C_1–O_1	1·27	O_1–C_1–O_2	122
C_1–O_2	1·21	C_3–C_2–N	109
		C_1–C_2–N	110
C_5–${}_1C_5$	3·91		
C_5–${}_2C_5$	3·78	${}_1O_1$–N–${}_2O_1$	113
C_5–${}_3C_5$	4·81	C_2–N–${}_1O_1$	108
S–${}_1C_5$	4·13	C_2–N–${}_2O_1$	110
S–${}_2C_5$	4·01	C_2–N–${}_1O_2$	108
N–${}_1O_1$	2·82	C_1–O_2–${}_1$N	128
N–${}_2O_1$	2·80	C_1–O_1–${}_2$N	136
N–${}_1O_2$	2·78	C_1–O_1–${}_3$N	103

Discussion

The molecular dimensions and intermolecular bonding in both α and β forms of methionine are so alike that the crystal structures will be considered together.

The high discrepancies for all reflexions can be partly related to the difficulty of accurate intensity measurement for plate-like crystals. However, additional factors may be noted in Figs. 3 and 8. First, the sulphur atom is elliptical in projection, indicating that there is preferred vibration perpendicular to the main chain direction. Secondly, the peak heights decrease from C_2 to C_5 (e.g. for α-methionine, the values are 9·0, 8·5, 8·0 to 7·2 e.Å^{-2}) and their shapes tend to be slightly elongated in the same direction as that of the sulphur atom. There is therefore considerable thermal motion in the parts of the molecule distant from $CH.NH_3^+.COO^-$. This effect of preferred vibration modes on peak heights has been noted in geranylamine hydrochloride (Jeffreys, 1945) and in anthracene (Sinclair, Robertson & Mathieson, 1950). To obtain a better correlation with observed structure amplitudes, different asymmetric temperature corrections to the scattering curves would be required for these atoms but were not deemed necessary since the amplitudes of terms do not reach a sufficiently low value for these factors to modify any calculated signs.

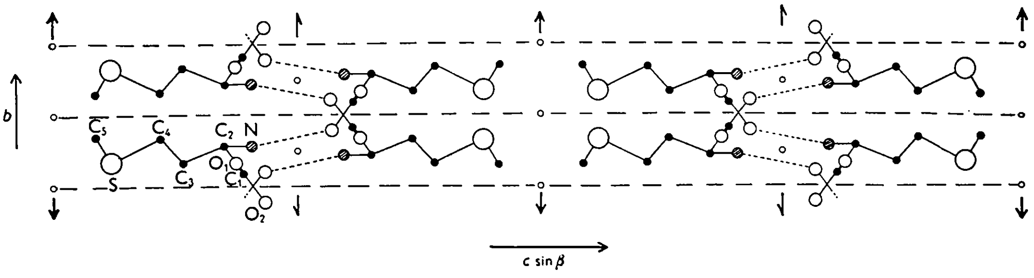

Fig. 10. The crystal structure of β-methionine projected down the *a* axis. Scale: 1 cm. = 2·5 Å.

Table 5. *Comparison of observed and calculated structure amplitudes*

α-Methionine

hkl	F_o	F_c
001	39	−47
002	< 3	4
003	5	2
004	93	−94
005	36	29
006	72	−55
007	22	21
008	55	42
009	< 6	4
0,0,10	12	− 8
0,0,11	19	−20
0,0,12	21	−23
0,0,13	8	− 6
0,0,14	16	15
0,0,15	18	16
0,0,16	13	14
0,0,17	< 8	4
0,0,18	< 8	3
0,0,19	7	−10
0,0,20	< 6	9
0,0,21	< 4	6
$2,0,\overline{21}$	28	17
$2,0,\overline{20}$	< 6	4
$2,0,\overline{19}$	7	6
$2,0,\overline{18}$	12	−10
$2,0,\overline{17}$	8	−12
$2,0,\overline{16}$	< 8	− 1
$2,0,\overline{15}$	8	−10
$2,0,\overline{14}$	< 8	2
$2,0,\overline{13}$	27	23
$2,0,\overline{12}$	22	15
$2,0,\overline{11}$	15	−13
$2,0,\overline{10}$	17	−13
$20\overline{9}$	51	46
$20\overline{8}$	15	− 7
$20\overline{7}$	< 5	6
$20\overline{6}$	43	40
$20\overline{5}$	70	66
$20\overline{4}$	19	7
$20\overline{3}$	45	35
$20\overline{2}$	30	−39
$20\overline{1}$	47	−41
200	93	−74
201	< 4	− 2
202	75	64
203	18	22
204	32	−12
205	11	−14
206	6	− 6
207	40	−46
208	< 6	3
209	< 7	− 5
2,0,10	41	42
2,0,11	27	32
2,0,12	13	−11
2,0,13	13	11
2,0,14	25	−24
2,0,15	< 8	11
2,0,16	< 8	− 2
2,0,17	< 7	− 2
2,0,18	< 7	8
2,0,19	< 6	4
2,0,20	< 4	2
$4,0,\overline{21}$	14	− 7
$4,0,\overline{20}$	< 6	2
$4,0,\overline{19}$	11	11
$4,0,\overline{18}$	16	11
$4,0,\overline{17}$	< 8	− 4
$4,0,\overline{16}$	< 8	1
$4,0,\overline{15}$	16	−17
$4,0,\overline{14}$	8	−11
$4,0,\overline{13}$	8	− 5
$4,0,\overline{12}$	27	−22
$4,0,\overline{11}$	51	56
$4,0,\overline{10}$	17	20
$40\overline{9}$	13	13
$40\overline{8}$	14	12
$40\overline{7}$	50	−50
$40\overline{6}$	13	− 4
$40\overline{5}$	47	37
$40\overline{4}$	< 5	10
$40\overline{3}$	23	16
$40\overline{2}$	27	29
$40\overline{1}$	< 5	5
400	24	−16
401	12	−17
402	83	−72
403	33	26
404	24	23
405	14	24
406	39	32
407	< 7	0
408	< 7	6
409	12	−19
4,0,10	30	−33
4,0,11	< 8	− 1
4,0,12	13	12
4,0,13	< 8	4
4,0,14	8	10
4,0,15	< 7	− 6
4,0,16	< 7	0
4,0,17	< 6	7
4,0,18	< 5	8
$6,0,\overline{20}$	< 5	− 6
$6,0,\overline{19}$	22	−15
$6,0,\overline{18}$	< 7	0
$6,0,\overline{17}$	< 7	4
$6,0,\overline{16}$	17	16
$6,0,\overline{15}$	18	13
$6,0,\overline{14}$	< 8	2
$6,0,\overline{13}$	< 8	6
$6,0,\overline{12}$	< 8	− 4
$6,0,\overline{11}$	33	−31
$6,0,\overline{10}$	12	− 9
$60\overline{9}$	14	9
$60\overline{8}$	18	19
$60\overline{7}$	19	18
$60\overline{6}$	18	−17
$60\overline{5}$	13	7
$60\overline{4}$	31	−38
$60\overline{3}$	14	−15
$60\overline{2}$	< 7	− 2
$60\overline{1}$	< 7	5
600	56	57
601	7	4
602	34	26
603	10	−16
604	34	−36
605	< 8	− 4
606	< 8	− 8
607	< 8	6
608	< 8	10
609	< 8	11
6,0,10	< 8	1
6,0,11	< 8	− 5
6,0,12	19	−15
6,0,13	< 7	1
6,0,14	10	10
6,0,15	< 6	0
$8,0,\overline{18}$	< 5	− 3
$8,0,\overline{17}$	< 6	− 8
$8,0,\overline{16}$	11	− 9
$8,0,\overline{15}$	< 7	1
$8,0,\overline{14}$	< 8	0
$8,0,\overline{13}$	< 8	9
$8,0,\overline{12}$	< 8	5
$8,0,\overline{11}$	< 8	0
$8,0,\overline{10}$	8	7
$80\overline{9}$	45	−43
$80\overline{8}$	< 8	− 3
$80\overline{7}$	< 8	7
$80\overline{6}$	< 8	6
$80\overline{5}$	37	36
$80\overline{4}$	13	− 3
$80\overline{3}$	17	17
$80\overline{2}$	< 8	− 4
$80\overline{1}$	33	−34
800	< 8	−10
801	< 8	− 4
802	< 8	6
803	18	19
804	< 8	2
805	< 8	− 8
806	< 8	−10
807	15	−14
808	< 7	3
809	< 7	4
8,0,10	< 7	9
8,0,11	< 6	11
8,0,12	< 6	7
8,0,13	< 5	1
$10,0,\overline{16}$	< 4	2
$10,0,\overline{15}$	< 5	− 8
$10,0,\overline{14}$	< 6	− 9
$10,0,\overline{13}$	< 6	− 1
$10,0,\overline{12}$	< 7	− 4
$10,0,\overline{11}$	16	13
$10,0,\overline{10}$	< 7	6
$10,0,\overline{9}$	14	18
$10,0,\overline{8}$	< 8	4
$10,0,\overline{7}$	17	−18
$10,0,\overline{6}$	< 8	− 7
$10,0,\overline{5}$	< 8	− 9
$10,0,\overline{4}$	< 8	4
$10,0,\overline{3}$	< 8	1
$10,0,\overline{2}$	< 8	9
$10,0,\overline{1}$	< 8	5
10,0,0	< 8	1
10,0,1	12	−14
10,0,2	9	−15
10,0,3	< 7	5
10,0,4	< 7	− 1
10,0,5	< 7	13
10,0,6	< 6	10
10,0,7	< 6	2
10,0,8	< 5	3
011	30	30
012	18	−27
013	46	40
014	22	−20
015	6	− 5
016	26	20

Table 5 (*cont.*)

hkl	F_o	F_c
017	10	-16
018	16	14
019	8	10
0,1,10	9	2
0,1,11	< 9	5
0,1,12	9	8
0,1,13	12	-10
0,1,14	< 8	-2
0,1,15	13	-12
0,1,16	10	8
0,1,17	10	6
0,1,18	< 8	-4
0,1,19	7	6
0,1,20	< 6	-6
020	70	64
021	7	16
022	13	-6
023	13	-2
024	39	-40
025	< 5	-8
026	12	-12
027	8	11
028	27	20
029	10	9
0,2,10	< 9	-10
0,2,11	9	-12
0,2,12	13	-13
0,2,13	< 9	-10
0,2,14	< 9	11
0,2,15	14	13
0,2,16	< 9	11
0,2,17	10	9
0,2,18	< 7	-2
0,2,19	< 6	-7
031	19	18
032	18	13
033	17	14
034	9	-1
035	25	-25
036	17	-27
037	25	-19
038	18	13
039	18	-24
0,3,10	< 9	5
0,3,11	12	9
0,3,12	< 9	6
0,3,13	9	-11
0,3,14	9	-9
0,3,15	14	-15
0,3,16	12	10
0,3,17	< 7	11
0,3,18	< 6	-4
040	9	-11
041	9	12
042	< 9	3
043	< 9	-1
044	< 9	-5
045	12	-12
046	< 9	11
047	< 9	-2
048	< 9	-3
049	< 9	4
0,4,10	< 9	-4
0,4,11	< 9	-2
0,4,12	< 8	1
0,4,13	< 8	-6
0,4,14	< 7	3
0,4,15	< 6	3
0,4,16	< 6	-1

β-Methionine

hkl	F_o	F_c
002	74	-82
004	< 10	4
006	10	12
008	162	-208
0,0,10	44	28
0,0,12	152	-124
0,0,14	< 12	8
0,0,16	100	86
0,0,18	58	48
0,0,20	34	28
0,0,22	< 16	2
0,0,24	40	-32
0,0,26	58	-40
0,0,28	< 18	4
0,0,30	< 18	0
0,0,32	< 18	14
0,0,34	18	8
0,0,36	16	14
0,0,38	< 14	4
0,0,40	< 12	12
$2,0,\overline{42}$	38	32
$2,0,\overline{40}$	< 14	-4
$2,0,\overline{38}$	< 16	6
$2,0,\overline{36}$	34	-30
$2,0,\overline{34}$	26	-22
$2,0,\overline{32}$	< 14	-2
$2,0,\overline{30}$	20	-24
$2,0,\overline{28}$	< 18	12
$2,0,\overline{26}$	56	52
$2,0,\overline{24}$	54	40
$2,0,\overline{22}$	< 14	0
$2,0,\overline{20}$	< 16	-14
$2,0,\overline{18}$	62	-68
$2,0,\overline{16}$	16	-10
$2,0,\overline{14}$	18	-28
$2,0,\overline{12}$	30	34
$2,0,\overline{10}$	76	86
$20\overline{8}$	12	-8
$20\overline{6}$	46	68
$20\overline{4}$	46	-60
$20\overline{2}$	58	-64
200	170	-152
202	46	-62
204	136	116
206	106	98
208	26	46
2,0,10	46	38
2,0,12	52	48
2,0,14	62	-76
2,0,16	30	-46
2,0,18	94	-88
2,0,20	< 16	-8
2,0,22	36	50
2,0,24	< 18	0
2,0,26	64	68
2,0,28	< 18	6
2,0,30	< 18	-4
2,0,32	< 18	-6
2,0,34	16	-24
2,0,36	< 12	-8
2,0,38	< 10	-6
$4,0,\overline{42}$	22	-16
$4,0,\overline{40}$	< 12	-6
$4,0,\overline{38}$	32	22
$4,0,\overline{36}$	38	32
$4,0,\overline{34}$	< 18	10
$4,0,\overline{32}$	18	20
$4,0,\overline{30}$	20	-18
$4,0,\overline{28}$	18	-28
$4,0,\overline{26}$	32	-32
$4,0,\overline{24}$	88	-102
$4,0,\overline{22}$	60	-62
$4,0,\overline{20}$	26	32
$4,0,\overline{18}$	36	36
$4,0,\overline{16}$	82	92
$4,0,\overline{14}$	46	-46
$4,0,\overline{12}$	62	52
$4,0,\overline{10}$	80	-84
$40\overline{8}$	74	-68
$40\overline{6}$	40	-26
$40\overline{4}$	12	12
$40\overline{2}$	36	52
400	16	42
402	92	78
404	112	-100
406	< 14	-18
408	< 14	-20
4,0,10	36	-36
4,0,12	32	30
4,0,14	< 16	6
4,0,16	34	56
4,0,18	40	46
4,0,20	26	-32
4,0,22	34	-34
4,0,24	< 18	-16
4,0,26	32	-28
4,0,28	< 18	4
4,0,30	< 16	8
4,0,32	< 14	12
4,0,34	14	24
$6,0,\overline{40}$	< 12	2
$6,0,\overline{38}$	20	-18
$6,0,\overline{36}$	< 16	-10
$6,0,\overline{34}$	< 18	-14
$6,0,\overline{32}$	< 18	6
$6,0,\overline{30}$	< 18	20
$6,0,\overline{28}$	20	16
$6,0,\overline{26}$	26	36
$6,0,\overline{24}$	34	32
$6,0,\overline{22}$	38	-44
$6,0,\overline{20}$	52	-60
$6,0,\overline{18}$	34	-44
$6,0,\overline{16}$	16	-22
$6,0,\overline{14}$	42	34
$6,0,\overline{12}$	< 16	-2
$6,0,\overline{10}$	90	98
$60\overline{8}$	42	50
$60\overline{6}$	< 16	6
$60\overline{4}$	< 16	-18
$60\overline{2}$	96	-108
600	16	-8
602	64	-56
604	20	28
606	40	60
608	< 18	4
6,0,10	22	34
6,0,12	< 18	-4
6,0,14	< 18	-14
6,0,16	24	-34
6,0,18	< 18	-16
6,0,20	< 18	-2
6,0,22	26	34

Table 5 (*cont.*)

hkl	F_o	F_c
6,0,24	< 16	10
6,0,26	< 16	−12
6,0,28	18	16
8,0,$\overline{38}$	16	14
8,0,$\overline{36}$	< 14	8
8,0,$\overline{34}$	16	12
8,0,$\overline{32}$	< 16	2
8,0,$\overline{30}$	< 18	− 6
8,0,$\overline{28}$	18	−20
8,0,$\overline{26}$	< 18	−14
8,0,$\overline{24}$	< 20	− 6
8,0,$\overline{22}$	< 20	0
8,0,$\overline{20}$	66	74
8,0,$\overline{18}$	< 18	− 6
8,0,$\overline{16}$	< 18	− 6
8,0,$\overline{14}$	< 18	4
8,0,$\overline{12}$	58	−62
8,0,$\overline{10}$	18	6
80$\overline{8}$	28	−30
80$\overline{6}$	< 18	4
80$\overline{4}$	76	82
80$\overline{2}$	< 18	24
800	< 18	24
802	< 18	4
804	32	−42
806	< 20	−24
808	28	−32
8,0,10	< 18	−16
8,0,12	< 18	24
8,0,14	< 18	8
8,0,16	24	34
8,0,18	< 16	12
8,0,20	< 16	−10
8,0,22	< 12	−10
10,0,$\overline{36}$	< 8	− 4
10,0,$\overline{34}$	26	−22
10,0,$\overline{32}$	< 12	2
10,0,$\overline{30}$	14	16
10,0,$\overline{28}$	< 16	12
10,0,$\overline{26}$	24	32
10,0,$\overline{24}$	18	−10
10,0,$\overline{22}$	< 18	− 2
10,0,$\overline{20}$	26	−28
10,0,$\overline{18}$	18	−26
10,0,$\overline{16}$	18	20
10,0,$\overline{14}$	18	−12
10,0,$\overline{12}$	< 18	20
10,0,$\overline{10}$	< 18	12
10,0,$\overline{8}$	< 18	14
10,0,$\overline{6}$	< 18	− 2
10,0,$\overline{4}$	18	−34
10,0,$\overline{2}$	18	−24
10,0,0	< 18	4
10,0,2	< 18	20
10,0,4	< 16	0
10,0,6	< 16	28
10,0,8	< 16	6
10,0,10	< 14	− 6
10,0,12	< 14	− 8
10,0,14	14	−30
011	54	42
013	42	−42
015	44	48
017	84	−68
019	< 12	0
0,1,11	36	−32
0,1,13	18	12
0,1,15	44	52
0,1,17	14	18
0,1,19	10	6
0,1,21	< 12	0
0,1,23	< 12	− 4
0,1,25	24	36
0,1,27	12	−12
0,1,29	16	−22
0,1,31	22	22
0,1,33	16	20
0,1,35	< 10	0
0,1,37	12	22
0,1,39	8	−12
020	132	−114
022	< 14	−10
024	24	20
026	28	−14
028	78	70
0,2,10	< 14	10
0,2,12	26	16
0,2,14	32	20
0,2,16	62	−64
0,2,18	< 14	−10
0,2,20	14	−16
0,2,22	< 14	− 4
0,2,24	< 14	22
0,2,26	< 14	18
0,2,28	< 14	10
0,2,30	< 14	− 8
0,2,32	< 14	2
0,2,34	< 14	−16
0,2,36	< 12	− 4
0,2,38	< 10	− 6
031	46	−40
033	< 16	−10
035	< 16	12
037	30	28
039	54	54
0,3,11	18	24
0,3,13	< 18	− 8
0,3,15	54	−64
0,3,17	28	−44
0,3,19	< 16	10
0,3,21	26	−20
0,3,23	20	24
0,3,25	28	40
0,3,27	32	26
0,3,29	34	28
0,3,31	36	−34
0,3,33	22	−24
0,3,35	< 12	− 8
040	42	−44
042	< 18	10
044	< 18	0
046	20	10
048	20	16
0,4,10	< 16	8
0,4,12	< 16	26
0,4,14	< 16	0
0,4,16	< 16	−12
0,4,18	< 16	− 8
0,4,20	< 16	−12
0,4,22	< 16	− 2
0,4,24	< 16	8
0,4,26	< 14	0
0,4,28	< 12	4
0,4,30	< 12	− 2
051	< 16	12
053	16	20
055	16	−20
057	16	2
059	< 16	24
0,5,11	< 16	−12
0,5,13	< 16	12
0,5,15	< 16	12
0,5,17	< 15	20
0,5,19	< 14	− 4
0,5,21	< 13	12
0,5,23	< 12	− 6

The configuration of the group $CH.NH_3^+.COO^-$ in the methionine molecule is similar to that in the other α-amino acids analysed. In both forms, the nitrogen atom lies 0·70 Å out of the plane passing through $C_1C_2O_1O_2$, a distance greater than that observed in glycine (Albrecht & Corey, 1939) and alanine (Donohue, 1950). In both α- and β-methionine, the atoms C_1, C_2, C_3, C_4 and S form an almost planar zigzag chain. For α-methionine, C_5 by the free rotation of the bond C_5–S lies out of this plane, whereas for β-methionine it is in the plane.

As with the other α-amino acids investigated, the molecules of methionine in both forms are disposed in a manner that permits maximum hydrogen bonding between adjacent molecules. By reference to Fig. 11 it will be noted that each nitrogen atom is bonded to three adjacent oxygen atoms, the arrangement of all four bonds around this nitrogen being approximately tetrahedral if it is assumed that the hydrogen atom lies on the line joining the two atoms concerned. Thus two layers of methionine molecules are stabilised by interlinking infinite helices and zigzag chains of hydrogen bonds into a double-layer unit extending parallel to (001). The double-layer units are then stacked together by the neat packing of the end group CH_3–S into triads of related terminal CH_3 groups of the adjoining double layer. These packing arrangements in α- and β-methionine will be considered in greater detail in the next section.

In the *b* axis projections, C_1 and O_2 are incompletely

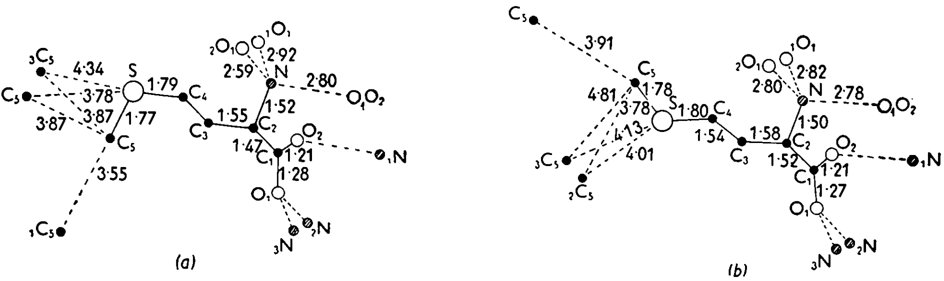

Fig. 11. Diagram to illustrate the relationship of one molecule with relevant atoms of neighbouring molecules: (*a*) α- methionine, (*b*) β-methionine.

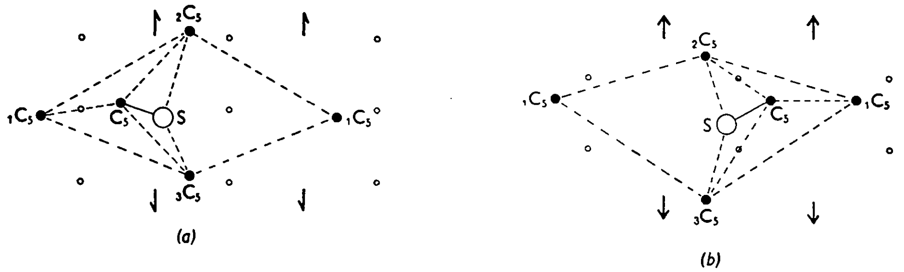

Fig. 12. Comparisons of packing of CH_3–S group with adjacent CH_3 groups, viewed perpendicular to (001): (*a*) α-methionine, (*b*) β-methionine.

resolved, but their atomic centres can be located with reasonable accuracy. In the *a* axis projections, the atoms C_2, C_1, N and O_1 overlap and O_2 is obscured by its symmetry-related atom. The *y* parameters of these atoms are less reliable than those of the remaining atoms. The probable error in intra-molecular bond lengths is 0·04 Å.

The average S–C bond length of 1·78 Å is less than the sum of the single-bond radii (1·81 Å) but is in good agreement with other recorded values (Mathieson & Robertson, 1949; see references on C–S bond lengths). The bond lengths for C–N in both structures (1·50 Å and 1·52 Å) are, within experimental error, in accord with the more precise values determined in DL-alanine (Donohue, 1950) and L-threonine (Shoemaker, Donohue, Schomaker & Corey, 1950). The difference in the bond lengths of C_1–O_1 (1·27 Å) and C_1–O_2 (1·21 Å) is of interest in relation to the system of hydrogen bonds. In the investigation of DL-alanine, Donohue has noted that when two hydrogen bonds are associated with one oxygen atom, O_1, (of a carboxyl group) and only one with the other oxygen atom, O_2, (all hydrogen bond lengths being equal), one resonance structure is stabilized and the distance C_1–O_2 approximates to that of a C–O double-bond value, viz., 1·19 Å (Goldschmidt & Llewellyn, 1950).

The C–C distances show rather marked variation from the normal single-bond value 1·54 Å, particularly for C_1–C_2. The alternation of bond lengths along the chain C_1 to C_5, including the C–S bonds in both cases, may be worthy of note. A similar alternation is observed in L-threonine and may be associated with the modification of the configuration of the carboxyl group by the asymmetric hydrogen bonding. The bond lengths in the present study are not sufficiently precise to permit any degree of certainty, but analogous variations have been observed in aliphatic dicarboxylic acids, again associated with asymmetry of the carboxyl group (Morrison & Robertson, 1949).

The NH---O distances are in close accord with values recorded for other α-amino acids. The mean distance in α-methionine is 2·77 Å and in β-methionine 2·80 Å.

Comparison of the terminal group packing in the dimorphs

The dominant factor in the crystal structures of the aliphatic α-amino acids is the extensive hydrogen bonding between the NH_3^+ and COO^- groups. This provides a stable network of hydrogen bonds between the molecules of the double-layer unit. The mode of stacking of the layers is governed, however, by the shape of the end portion of the aliphatic chain and their consequent packing with similar parts of the adjacent layers. For the two forms of methionine this is made clear in Fig. 12 by comparison of the packing of the CH_3–S group with the three neighbouring CH_3 groups. The relevant atoms are shown as viewed perpendicular to the (001) plane. It can be noted for both α- and β-methionine that the atoms C_5 are not far removed from a face-centred configuration. For α-methionine, the group C_5–S lies so that C_5 is equidistant from $_2C_5$ and $_3C_5$ at 3·87 Å and distant 3·55 Å from $_1C_5$. The sulphur atom lies at unequal distances from $_2C_5$ (4·33 Å) and $_3C_5^1$ (3·78 Å). In β-methionine, C_5–S is disposed so that the sulphur atom is almost equidistant from ${}_2C_5$ (4·02 Å) and ${}_3C_5$ (4·13 Å) and the distance C_5–${}_1C_5$ is 3·92 Å. C_5 then lies at distances from ${}_2C_5$ and ${}_3C_5$ of 3·78 and 4·81 Å respectively. It is clear that the mobile C_5–S bond can rotate to occupy two positions in which a balanced arrangement of van der Waals forces is achieved, the C_5–S group fitting into the triangle of atoms ${}_1C_5$, ${}_2C_5$ and ${}_3C_5$ in a manner akin to the packing of spheres in a hexagonal lattice. This arrangement may be described as distorted hexagonal packing.

Conclusion

The crystal structures of the dimorphs of methionine have been described. The system of hydrogen bonds binding the molecules in double layers is the same in both. The dimorphism of methionine is ascribed to the free rotation of the terminal CH_3–S group resulting in two different ways of achieving a stable balanced configuration of van der Waals forces. The two forms are therefore almost equally stable. The easy cleavage parallel to (001) is correlated with the weak forces between the double-layer units.

It may be deduced that one or other of these packing arrangements will be utilized in the crystal structures of the other straight-chain aliphatic α-amino acids, their space group being either $P2_1/a$ or $I2/a$ as observed (Dawson & Mathieson, 1951). It is probable that the different shapes of the end portion of the molecules of branched-chain acids do not permit the simple distorted hexagonal packing, and a stable configuration can be achieved only in the lower symmetry of the triclinic system.

On account of the equal stability of the dimorphs of methionine, it might be expected that disorder in stacking of layers could arise. Such disorder has not been observed in methionine, but was noted in the case of norleucine, the crystal structure of which will be reported later.

The author wishes to acknowledge assistance with some of the computations given by Mr N. Loukes.

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The Crystal Structure of Sodium Thiosulphate Pentahydrate

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The crystal structure of sodium thiosulphate pentahydrate has been determined by the use of three-dimensional Patterson methods and refined by two-dimensional Fourier synthesis.

The unit cell dimensions are $a=5{\cdot}94\pm0{\cdot}01$, $b=21{\cdot}57\pm0{\cdot}05$, $c=7{\cdot}53\pm0{\cdot}01$ Å, $\beta=103°\ 58'\pm5'$. The space group is $P2_1/c$. The structure shows a tetrahedral thiosulphate group, with a S–S distance of 1·97 Å and an average S–O distance of 1·48 Å. Each sodium atom is surrounded by an octahedral group of atoms; the external sulphur atom is one member of one such group, but the remainder are oxygens of the thiosulphate groups or are water oxygens. These octahedral groups share edges with each other to form chains parallel to the a axis, and these chains are linked together sideways by sharing oxygens with, and by hydrogen bonding to, the S_2O_3 groups.

Introduction

No structure determination of a compound containing the S_2O_3'' group has yet been reported, although determinations of salts of several other sulphur-oxygen anions have been carried through, principally by W. H. Zachariasen and co-workers (Zachariasen, 1932, 1934; Zachariasen & Buckley, 1931; Zachariasen & Ziegler, 1932; Zachariasen & Mooney, 1934; Helwig, 1932; Huggins, 1933). The shapes found for these anions suggest the probable nature of the S_2O_3'' group