Structure determination of L$_s$-threonine by neutron diffraction

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Abstract. The structure of the aminoacid, L$_s$-threonine [NH$_3^+$ CH(CHOHCH$_3$)COO$^-$], space group $P2_12_12_1$, $a=13\cdot630(5)$, $b=7\cdot753(1)$, $c=5\cdot162(2)$ Å, $z=4$, has been determined from neutron diffraction data using direct methods. The intensities of 1148 neutron Bragg reflections were measured from a single crystal. The structural parameters were refined by the method of least squares using anisotropic temperature factors. The final $R(F^2)$ is 0·068. The structure was also refined from the x-ray data of Shoemaker *et al* (1950 *J. Am. Chem. Soc.* **72** 2328); there is good agreement between the two sets of heavy atom parameters. The parameters of hydrogen atoms are of course more precisely determined in our neutron study. The molecular conformation and the hydrogen bonding scheme are discussed. Weighted average values of bond distances and angles from 14 aminoacid structures with ionized carboxylic groups studied by neutron diffraction at Brookheven and Trombay are also presented.

Keywords. L$_s$-threonine; neutron diffraction; hydrogen bonding; direct methods.

1. Introduction

The x-ray diffraction structure determination of L$_s$-threonine [NH$_3^+$CH(CHOHCH$_3$)COO$^-$] was carried out by Shoemaker *et al* (1950). In this study, only approximate hydrogen atom positions were found. We undertook the neutron diffraction investigation of this crystal to obtain precise nuclear positions for the hydrogen atoms. This work is the fifth in a series of such studies on aminoacids and their derivatives in our laboratory.*

2. Experimental

Single crystals of L$_s$-threonine were grown by slow evaporation from an aqueous solution of the compound. The crystals obtained were prisms elongated along the c-axis with {110} as the side faces. One such crystal weighing 12 mg was chosen for data collection. This was a parallelopiped of dimensions $5\cdot36 \times 1\cdot62 \times 1\cdot06$ mm with the longest dimension along the c-axis. This was mounted on the 4-circle neutron diffractometer 3D-FAD (Momin *et al* 1969) at the CIRUS reactor in Trombay. The intensity data were collected using a neutron beam of wavelength 1·178 Å, obtained by reflection from the (511) plane of a Ge single crystal. The cell constants

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*The other aminoacids so far studied in our laboratory are: L–asparagine·H$_2$O (Ramanadham *et al* 1972), L–glutamic acid·HCl (Sequeira *et al* 1972), L–lysine·HCl·2H$_2$O (Bugayong *et al* 1972), L–cysteic acid·H$_2$O (Ramanadham *et al* 1973) and L–cystine·2HCl (Gupta *et al* 1973).

were refined by least squares technique from optimised 2θ angles of 105 reflections, randomly distributed in reciprocal space. These refined values, $a=13\cdot630(5)$, $b=7\cdot753(1)$ and $c=5\cdot162(2)$ Å, compare well with the values $a=13\cdot611(20)$, $b=7\cdot738(8)$ and $c=5\cdot142(5)$ Å reported by Shoemaker *et al* (1950). The calculated density with four molecules in the unit cell comes out to be $1\cdot461$ gm cm^{-3} compared to the measured density of $1\cdot462$ gm cm^{-3}. The systematic absences confirmed the space group to be $P2_12_12_1$ as determined in the x-ray study.

The integrated neutron counts for 1152 Bragg reflections[†] consisting of 857 hkl, 211 $\bar{h}kl$, 82 $h\bar{k}l$ and $2\bar{h}k0$, having $\sin\theta/\lambda \leqslant 0\cdot68$ Å^{-1} were measured in the symmetrical setting of the diffractometer using $\theta-2\theta$ coupled step scan mode ($0\cdot1°$ step in 2θ). The background was scanned for a minimum of $1°$ on either side of the peaks. A standard reflection was recorded after every 15 measurements. The variation in the intensity of this standard reflection during the 4 months of data collection was within 4%.

Squared observed structure factors were obtained from the integrated intensities and then corrected for absorption with the calculated linear absorption coefficient $\mu=2\cdot86$ cm^{-1}. The transmission factors ranged from $0\cdot612$ to $0\cdot789$. The symmetry related reflections were not averaged. 32 reflections were found to be having negative F_0^2 values. These were omitted in Fourier calculations but included in the least squares refinement of the structure.

3. Structure determination by tangent formula

Sikka (1969) has shown that the direct methods involving the symbolic addition and tangent formula techniques (Karle and Karle 1966) are applicable to neutron diffraction structure determination if the relative scattering power of hydrogen atoms, $\sigma = \sum_{\text{H}} b_{\text{H}}^2 / \sum_{\text{all atoms}} b_{\text{i}}^2$ is less than 30%[‡]. In the case of L_s-threonine σ is 26% near the upper limit set by Sikka. Therefore, it was decided to determine the structure of L_s-threonine by direct methods as a further test of the applicability of these methods in neutron diffraction.[§]

Normalized structure factors, E's were derived from $|F_0|$ by the formula

$$|E| = \frac{|F_0|}{[\varepsilon\langle I\rangle]^{\frac{1}{2}}} \qquad (1)$$

Here ε is a factor which takes into account the enhanced $|F_0|$ values for some reflections due to space group symmetry and $\langle I\rangle$ is the local average intensity, which was

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[†]Four reflections (322), (14 4 1), (11 7 0) and (393) were dropped from the data set as they were misset during the data collection.

[‡]Since this proposal three structures, L–proline·H_2O (Verbist *et al* 1972), L–serine·H_2O (Frey *et al* 1973) and melampodin (Bernal and Wilkins 1972), have been solved by this method from neutron data. The σ values for these structures are 27%, 26% and 22% respectively.

[§]In order to retain the objectivity of this approach, none of the authors studied the x-ray paper on L_s-threonine by Shoemaker *et al* (1950) till the structure was solved from neutron data, apart from noting the crystal data.

Table 1. Set of initial phases for multi-solution tangent formula computations.

h k l	$\mid E \mid$	ϕ	weight	
3 1 4	2·628	45°	1·0	For fixing origin and enantiomorph
17 4 0	2·109	90	1·0	
12 0 1	2·443	90	1·0	
6 2 0	2·112	180	0·837	From Σ_1 relation
16 2 0	2·716	180	0·592	
0 8 4	1·758	180	0·515	
14 6 0	2·223	0	0·422	
0 2 4	1·743	180	0·345	
8 4 0	1·878	180	0·236	
0 8 1	2·237	0 or 180	1·0	For multi-solution
4 0 3	1·897	±90	1·0	

estimated by the K-plot technique of Karle and Hauptman (1953).* The observed distribution values of $\langle \mid E \mid \rangle = 0·85$ and $\langle \mid E^2 - 1 \mid \rangle = 0·75$ agree well with the theoretical values of $0·89$ and $0·74$ respectively for the non-centrosymmetric case. The phases were determined by the multisolution tangent formula method of Germain and Woolfson (1968). 175 reflections with $\mid E \mid \geqslant 1·3$ were used. The starting set of reflections for generating the different tangent formula phase sets are given in table 1. These include 3 reflections for fixing the origin and enantiomorph chosen according to the rules given by Hauptman and Karle (1956), six Σ_1 reflections and two (081) and (403) which can take 0 or π and $\pi/2$ or $-\pi/2$ respectively as their phase values. The weighted tangent formula (Germain, Main and Woolfson 1971)

$$\tan \phi_H = \frac{T}{B} = \frac{\left[\sum_K w_K w_{H-K} \mid E_K E_{H-K} \mid \sin (\phi_K + \phi_{H-K}) \right]}{\left[\sum_K w_K w_{H-K} \mid E_K E_{H-K} \mid \cos (\phi_K + \phi_{H-K}) \right]} \qquad (2)$$

was used for calculations.

The weights were chosen as

$$w = \tanh (0·5 a_H) \text{ for } a_H \geqslant 2·0$$
$$= 0 \qquad\qquad \text{ for } a_H < 2·0 \qquad\qquad (3)$$

Here $\quad a_H = \dfrac{2\beta_3}{\beta_2^{3/2}} \left[\mid E_H \mid \sum_H (T^2 + B^2)^{\frac{1}{2}} \right] \quad$ and

$$\beta_n = \sum_{\text{all atoms}} b_j^n$$

The weights for the initial sets are given in table 1. For Σ_1 reflections, $w = 2P_H - 1$ where P_H is the probability that the sign is correctly determined by the Σ_1 relation.

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*Considerable difficulty was encountered in applying the Wilson plot method (Wilson 1942) for obtaining the scale factor and the average isotropic temperature factor. This was due to extinction effects for the low angle data and curving of the linear plot for the high angle data. The latter is due to, perhaps, sharper decrease in the hydrogen contribution to the high angle reflections as a result of higher B values and lower scattering amplitude of hydrogen atoms compared to other atoms in the structure.
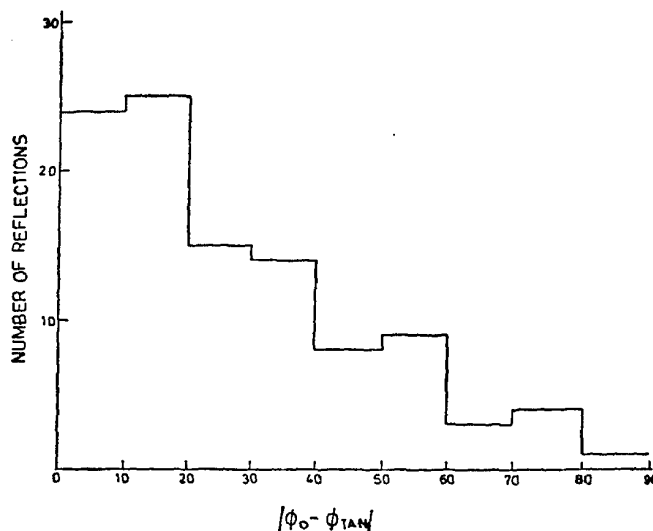
Figure 1. Frequency distribution of the error $|\phi_0 - \phi_{\mathrm{TAN}}|$ for non-centrosymmetric reflections in L$_S$-threonine. Five reflections had errors greater than 90°. Seven out of fifty-six centrosymmetric reflections had errors of 180°.

The set for which the phases of (081) and (403) were 0 and $-\pi/2$, gave the highest figure of merit and an E map was computed from the phases of this set. In this map, the five highest peaks which made chemical sense were chosen as nuclear sites. A structure factor calculation followed by a Fourier synthesis revealed the three remaining heavy atoms. Finally the nine hydrogen atoms were located from a difference Fourier map. The R value $\left(= \dfrac{\Sigma\,|\,|F_0|-|F_c|\,|}{\Sigma\,|F_0|} \right)$ at this stage was 0·36.

A comparison with the x-ray coordinates showed that we had obtained a set related to the former by the transformation: $\frac{1}{2}-x$, $\frac{1}{2}-y$, $z-\frac{1}{2}$ and that all the atoms were correctly positioned. Figure 1 shows in histogram form, the distribution of $|\phi_0 - \phi_{\mathrm{TAN}}|$ for non-centrosymmetric reflections. Here ϕ_0 is phase calculated from the final least square parameters and ϕ_{TAN} is the tangent-formula calculated phase. Only 7 out of 56 reflections whose phases were fixed by space group to be 0, π and $\pm\pi/2$, were in error by 180°. The average mean error in phases is 28°. The phase of the (314) reflection, which was used to fix the enantiomorph was found to have $\phi_0 = -43°$. This means that enantiomorph opposite to that fixed by us was obtained by using ϕ_{TAN}'s. This result confirms the observation of Hauptman and Duax (1972) that one reflection may not be sufficient for choosing the enantiomorph.

4. Structure refinement

The structural parameters obtained in the last section were subjected to a series of isotropic and anisotropic full-matrix least squares refinements. The nuclear scattering lengths used were: $b_N=0·94$, $b_C=0·664$, $b_O=0·58$ and $b_H=-0·374\times10^{-12}$ cm (Bacon 1972). All 1148 reflections were included in the refinements. The function minimized was $\Sigma w\,|\overline{F_0^2}-|F_C|^2\,|^2$ where w is the weight. In the initial stages, w was taken to be $1/\sigma(F_0^2)$ where $\sigma(F_0^2)$ were derived from counting statistics. Near the end of the refinements, an error analysis was done and the following weighting scheme was obtained:

$$w^{-\frac{1}{2}} = \langle\,|\Delta F^2|^2\,\rangle^{\frac{1}{2}} = 0·967 - 0·01802\,|F_0|^2 + 0·0005644\,|F_0|^4 \qquad (4)$$

Table 2. Atomic parameters for L_s-threonine. First row for each atom corresponds to neutron parameters. Second row corresponds to x-ray parameters. All the parameters are multiplied by 10^5 except positional parameters of hydrogen atoms from x-ray refinement which are multiplied by 10^4. The estimated standard deviations in units of the least significant digit are given in parentheses. The expression for the temperature factor is $\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C	49585(19)	18436(31)	29901(49)	156(11)	615(33)	1352(84)	-95(18)	67(28)	-14(52)
	49573(24)	18429(37)	29795(58)	279(14)	876(42)	2155(119)	-80(26)	12(41)	-201(63)
C^α	39837(16)	10601(29)	39281(51)	135(11)	498(32)	1411(88)	-51(14)	25(25)	-63(48)
	39841(21)	10618(37)	39202(60)	263(15)	899(43)	1830(113)	-48(23)	-25(34)	-69(64)
C^β	31795(18)	24267(33)	43141(51)	180(11)	612(36)	1607(100)	44(16)	56(26)	-119(58)
	31803(22)	24203(39)	42954(64)	282(15)	978(44)	2426(120)	1(24)	117(35)	95(73)
C'^2	29919(22)	33642(46)	18388(75)	317(15)	1178(54)	2427(130)	195(24)	48(42)	567(73)
	29085(28)	33628(53)	18309(88)	419(18)	1541(61)	3460(162)	108(33)	98(52)	821(100)
N	41392(13)	1263(24)	64179(36)	183(9)	626(29)	1748(74)	3(15)	70(23)	309(42)
	41375(18)	1347(33)	64157(57)	267(13)	913(40)	2250(109)	-6(22)	33(34)	145(57)
O^1	55753(22)	21641(52)	46819(66)	203(13)	1795(74)	1789(112)	-357(28)	19(34)	-101(83)
	55791(16)	21681(34)	46725(50)	331(12)	1968(54)	2631(101)	-312(21)	-46(29)	29(62)
O^2	50338(24)	21127(46)	5947(56)	332(17)	1353(64)	966(108)	-276(29)	42(39)	40(63)
	50284(19)	21132(29)	5940(44)	435(13)	1509(45)	2187(89)	-263(24)	143(31)	30(52)
O'^1	23686(22)	14834(42)	52819(74)	165(15)	986(53)	3141(156)	94(22)	220(38)	492(79)
	23645(17)	14642(29)	52876(55)	235(11)	1254(39)	3919(115)	112(18)	223(31)	521(57)
H^1	45494(42)	8551(75)	77071(121)	362(29)	1149(89)	2509(227)	-172(44)	-221(73)	292(138)
	4511(26)	899(48)	7569(74)						
H^2	34762(37)	-1394(82)	72590(115)	291(26)	1261(90)	2892(219)	-24(41)	238(66)	448(149)
	3587(30)	-130(49)	7304(71)						
H^3	44685(40)	-10482(74)	60432(118)	380(28)	1123(93)	2897(243)	220(44)	-59(75)	183(135)
	4426(27)	-892(49)	6031(80)						
H^α	37199(39)	1111(78)	25165(104)	353(29)	1127(82)	1976(182)	-173(46)	-98(57)	-387(138)
	3743(27)	235(45)	2682(70)						
H^β	34378(43)	33497(80)	58012(142)	478(34)	1035(88)	3334(249)	138(47)	-38(86)	-4467(128)
	3394(29)	3354(47)	5594(83)						
H'^1	17797(36)	22007(68)	54960(113)	254(24)	1211(97)	2371(218)	123(43)	141(61)	244(125)
	1939(28)	2062(51)	5442(77)						
H'^{21}	22492(62)	41359(117)	21711(215)	706(53)	2744(161)	5991(468)	849(84)	243(133)	2143(263)
	2376(35)	4113(62)	2170(104)						
H'^{22}	34921(62)	41983(119)	11884(206)	652(47)	2585(154)	6319(474)	-31(74)	-136(140)	2815(268)
	3465(38)	4159(68)	1240(108)						
H'^{23}	27272(65)	24428(138)	2589(178)	902(56)	2529(165)	3398(307)	331(101)	-433(119)	-140(228)
	2780(43)	2548(70)	316(100)						

Table 3. Structure Factor Table based on the refinement of the structure of L_S–threonine using neutron diffraction data. The five sub-columns in each column are h, k, l, $100\times F_O^2$ and $100\times|F_C|^2$ respectively.

2	0	0	3328	3296
-2	0	0	3397	3296
4	0	0	3306	3284
-4	0	0	3387	3284
6	0	0	2130	2127
-6	0	0	2144	2127
8	0	0	104	71
-8	0	0	116	71
10	0	0	16128	15474
-10	0	0	15978	15474
12	0	0	4540	4618
-12	0	0	4679	4618
14	0	0	222	109
-14	0	0	214	109
16	0	0	486	540
-16	0	0	582	540
18	0	0	65	96
1	1	0	738	742
-1	1	0	783	742
1	-1	0	901	742
2	1	0	604	642
-2	1	0	656	642
2	-1	0	614	642
3	1	0	128	117
-3	1	0	128	117
3	-1	0	120	117
4	1	0	2078	2030
-4	1	0	2100	2030
4	-1	0	1996	2030
5	1	0	168	140
5	-1	0	167	140
6	1	0	96	101
7	1	0	4483	4663
7	-1	0	4879	4663
8	1	0	530	672
9	1	0	1333	1381
9	-1	0	1438	1381
10	1	0	572	657
11	1	0	89	98
12	1	0	5518	5606
12	-1	0	5462	5606
13	1	0	4194	4026
13	-1	0	3817	4026
14	1	0	12	23
15	1	0	1050	862
15	-1	0	727	862
16	1	0	90	79
17	1	0	-98	19
18	1	0	2	6
0	2	0	5712	5892
0	-2	0	5683	5892
1	2	0	4721	5051
-1	2	0	5013	5051
1	-2	0	5031	5051
2	2	0	337	315
-2	2	0	322	315
2	-2	0	347	315
3	2	0	344	348
3	-2	0	344	348
4	2	0	2420	2506
-4	2	0	2572	2506
4	-2	0	2595	2506
5	2	0	1188	1262
6	2	0	6053	5952
-6	2	0	6154	5952
6	-2	0	6075	5952
7	2	0	3412	3469
7	-2	0	3437	3469
8	2	0	535	574
-8	2	0	587	574
8	-2	0	590	574
9	2	0	262	226
10	2	0	550	488
10	-2	0	456	488
11	2	0	4143	4151
11	-2	0	3993	4151
12	2	0	350	491
13	2	0	312	184
14	2	0	474	390
15	2	0	167	99
15	-2	0	259	99
16	2	0	3128	3150
16	-2	0	3022	3150
17	2	0	34	141
18	2	0	1423	1492
1	3	0	116	31
2	3	0	72	55
3	3	0	680	706
-3	3	0	667	706
3	-3	0	710	706
4	3	0	3799	3883
4	-3	0	3874	3883
5	3	0	2527	2604
5	-3	0	2612	2604
6	3	0	88	14
-6	3	0	76	14
6	-3	0	117	14
7	3	0	198	187
8	3	0	2748	2735
8	-3	0	2615	2735
9	3	0	5539	5312
-9	3	0	5486	5312
9	-3	0	5327	5312
10	3	0	320	257
11	3	0	61	0
12	3	0	325	276
-12	3	0	320	276
12	-3	0	366	276
13	3	0	149	190
14	3	0	93	5
15	3	0	302	382
15	-3	0	363	382
16	3	0	-9	2
17	3	0	28	39
0	4	0	274	299
0	-4	0	247	299
1	4	0	1610	1533
1	-4	0	1588	1533
2	4	0	3618	3849
-2	4	0	3847	3849
2	-4	0	3883	3849
3	4	0	2490	2444
3	-4	0	2443	2444
4	4	0	68	2
-4	4	0	105	2
4	-4	0	55	2
5	4	0	2286	2346
5	-4	0	2321	2346
6	4	0	-12	70
6	-4	0	122	70
7	4	0	2582	2497
7	-4	0	2405	2497
8	4	0	3946	4240
-8	4	0	4389	4240
8	-4	0	4239	4240
9	4	0	180	119
10	4	0	-52	21
11	4	0	581	512
12	4	0	462	454
-12	4	0	512	454
12	-4	0	476	454
13	4	0	194	248
14	4	0	277	137
15	4	0	1193	1268
15	-4	0	1299	1268
16	4	0	220	182
-16	4	0	186	162
16	-4	0	247	162
17	4	0	1798	1866
1	5	0	1024	1102
1	-5	0	1181	1102
2	5	0	364	323
3	5	0	240	270
4	5	0	561	570
5	5	0	1082	1076
-5	5	0	1085	1076
5	-5	0	1145	1076
-5	-5	0	1076	1076
6	5	0	96	60
7	5	0	412	339
8	5	0	9	40
9	5	0	203	253
10	5	0	919	968
-10	5	0	936	968
10	-5	0	946	968
11	5	0	185	226
12	5	0	276	64
13	5	0	272	206
14	5	0	1373	1421
14	-5	0	1535	1421
15	5	0	118	94
15	-5	0	71	94
16	5	0	364	195
0	6	0	1904	1887
0	-6	0	1906	1887
1	6	0	1793	1535
1	-6	0	1367	1535
2	6	0	116	125
3	6	0	174	133
-3	6	0	209	133
3	-6	0	165	133
4	6	0	4118	4126
4	-6	0	4023	4126
5	6	0	2477	2508
5	-6	0	2489	2508
6	6	0	1876	1940
-6	6	0	1957	1940
6	-6	0	2048	1940
-6	-6	0	2017	1940
7	6	0	30	2
8	6	0	92	29
9	6	0	32	1
9	-6	0	73	1
10	6	0	154	178
11	6	0	731	678
12	6	0	292	151
-12	6	0	237	151
12	-6	0	198	151
13	6	0	1054	1128
13	-6	0	1272	1128
14	6	0	1581	1371
15	6	0	563	519
1	7	0	94	130
2	7	0	710	626
3	7	0	559	550
4	7	0	165	137
5	7	0	1747	1707
5	-7	0	1721	1707
6	7	0	97	140
7	7	0	273	97
-7	7	0	193	97
7	-7	0	239	97
8	7	0	105	48
9	7	0	98	62
10	7	0	183	181
12	7	0	709	690
13	7	0	245	216
0	8	0	392	283
0	-8	0	394	283
1	8	0	543	366
2	8	0	420	341
3	8	0	88	137
4	8	0	1145	1131
-4	8	0	1126	1131
4	-8	0	1066	1131
5	8	0	497	471
6	8	0	859	873
7	8	0	230	130
8	8	0	950	1008
-8	8	0	1031	1008
8	-8	0	1097	1008
9	8	0	185	241
10	8	0	131	17
11	8	0	-4	4
12	8	0	82	134
1	9	0	198	63
2	9	0	458	496
3	9	0	162	227
4	9	0	145	0
5	9	0	82	23
6	9	0	60	56
7	9	0	590	563
8	9	0	26	24
9	9	0	1869	1790
9	-9	0	1750	1790
0	10	0	211	22
1	10	0	346	376
2	10	0	1335	1596
3	10	0	309	221
4	10	0	181	188
5	10	0	217	155
1	0	1	3046	3071
-1	0	1	3126	3071
2	0	1	1587	1542
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8	-3	4	1227	1262
9	3	4	1185	1158
9	-3	4	1256	1155
10	3	4	873	874
11	3	4	275	279
12	3	4	917	839
13	3	4	418	514
14	3	4	1100	1049
0	4	4	1601	1542
0	-4	4	1549	1542
1	4	4	1603	1637
1	-4	4	1615	1637
2	4	4	946	1062
3	4	4	878	828
4	4	4	116	27
-4	4	4	109	27
4	-4	4	49	27
5	4	4	0	46
6	4	4	98	163
7	4	4	84	70
8	4	4	152	19
-8	4	4	90	19
8	-4	4	133	19
9	4	4	280	207
10	4	4	397	181
11	4	4	103	105
12	4	4	394	358
12	-4	4	597	358
13	4	4	627	688
0	5	4	923	934
1	5	4	342	429
2	5	4	576	567
3	5	4	247	382
4	5	4	1238	1296
4	-5	4	1300	1296
5	5	4	89	37
6	5	4	436	474
7	5	4	42	11
8	5	4	1416	1474
8	-5	4	1477	1477
9	5	4	344	381
10	5	4	873	811
11	5	4	844	1074
12	5	4	44	112
0	6	4	36	38
1	6	4	340	340
2	6	4	131	97
3	6	4	-74	24
4	6	4	994	710
5	6	4	67	54
6	6	4	101	33
7	6	4	149	118
8	6	4	110	90
9	6	4	156	52
10	6	4	93	66
0	7	4	204	237
1	7	4	321	364
2	7	4	1167	1097
2	-7	4	1109	1097
3	7	4	448	403
4	7	4	18	72
5	7	4	18	376
6	7	4	-6	19
7	7	4	703	708
8	7	4	122	449
0	8	4	912	954
0	-8	4	834	954
1	8	4	371	232
2	8	4	302	230
3	8	4	350	65
4	8	4	771	879
5	8	4	44	31
1	0	5	2482	2764
-1	0	5	2731	2764
2	0	5	1416	1378
-2	0	5	1457	1378
3	0	5	388	477
4	0	5	304	173
5	0	5	14	30
-5	0	5	82	30
6	0	5	-61	0
7	0	5	-94	59
8	0	5	1207	1208
-8	0	5	1248	1208
9	0	5	331	204
10	0	5	132	17
-10	0	5	96	17
11	0	5	388	498
12	0	5	182	178
0	1	5	185	147
1	1	5	67	8
2	1	5	870	848
3	1	5	448	450
4	1	5	1344	1402
4	-1	5	1366	1402
5	1	5	1978	2035
5	-1	5	1924	2035
6	1	5	815	340
7	1	5	693	679
8	1	5	879	961
9	1	5	370	318
10	1	5	488	308
11	1	5	384	143
12	1	5	387	318
0	2	5	228	[illegible]
1	2	5	-26	55
2	2	5	418	374
3	2	5	1104	1160
3	-2	5	1160	1160
4	2	5	170	130
5	2	5	779	671
6	2	5	530	539
7	2	5	777	854
8	2	5	147	279
9	2	5	159	95
10	2	5	320	128
11	2	5	19	23
12	2	5	-64	18
0	3	5	522	520
1	3	5	856	961
2	3	5	1180	1081
2	-3	5	1007	1081
3	3	5	742	842
4	3	5	832	774
5	3	5	1332	1434
5	-3	5	1495	1434
6	3	5	231	67
7	3	5	100	82
8	3	5	440	137
9	3	5	150	190
10	3	5	1028	1216
11	3	5	258	198
0	4	5	256	285
1	4	5	978	1046
2	4	5	83	48
3	4	5	218	77
4	4	5	89	78
5	4	5	283	163
6	4	5	811	888
7	4	5	428	361
8	4	5	783	708
9	4	5	46	48
10	4	5	791	476
0	5	5	74	0
0	-5	5	183	0
1	5	5	786	748
2	5	5	221	190
3	5	5	384	496
4	5	5	258	59
5	5	5	128	14
-5	5	5	188	14
5	-5	5	190	14
6	5	5	432	306
7	5	5	161	140
8	5	5	873	771
9	5	5	1568	1588
0	6	5	1582	1444
1	6	5	-108	9
2	6	5	318	160
3	6	5	278	323
4	6	5	44	161
5	6	5	646	673
6	6	5	321	233
7	6	5	273	239
0	7	5	1388	1362
1	7	5	487	417
2	7	5	716	694
3	7	5	477	447
0	0	6	839	847
1	0	6	-84	4
2	0	6	-17	3
3	0	6	128	41
-3	0	6	49	41
4	0	6	278	21
5	0	6	788	861
-5	0	6	808	861
6	0	6	271	274
-6	0	6	184	274
7	0	6	172	116
8	0	6	361	19
9	0	6	308	98
0	1	6	181	181
1	1	6	234	74
2	1	6	841	136
3	1	6	430	399
4	1	6	387	33
5	1	6	982	63
6	1	6	147	43
7	1	6	187	24
8	1	6	88	92
9	1	6	43	178
0	2	6	922	884
1	2	6	164	87
2	2	6	132	183
3	2	6	684	804
4	2	6	59	217
5	2	6	80	291
6	2	6	384	281
7	2	6	202	307
8	2	6	-94	2
0	3	6	108	114
1	3	6	906	938
2	3	6	141	80
3	3	6	456	410
4	3	6	672	475
5	3	6	118	112
6	3	6	871	832
7	3	6	167	186
0	4	6	106	5
1	4	6	1298	1318
2	4	6	240	176
3	4	6	277	278
4	4	6	660	664
5	4	6	373	252
6	4	6	811	654
0	5	6	2180	2181
1	5	6	-35	19
2	5	6	160	343
3	5	6	638	635

Moderate extinction effects were noticed on a comparison of F_0^2's and $|F_C|^2$ (minimum $F_0^2 / |F_C|^2 = 0.70$). The Zachariasen (1967) extinction correction term was used.

$$y = (1+2x)^{-\frac{1}{2}} \tag{5}$$

$$x = G Q \overline{T} \tag{6}$$

$$Q = \frac{\lambda^3 \mathcal{N}_C^2 F_0^2 V}{\sin 2\theta} \tag{7}$$

$$\overline{T} = -\frac{1}{\mu} \frac{d\theta}{d\mu} \tag{8}$$

The parameter G was refined along with other structural parameters.

For the anisotropic refinement, the total number of variables was 155 (one scale factor, G, 51 positional and 102 temperature parameters). This refinement had to be done in two blocks with 137 parameters varied in any one cycle. The refinement was assumed to have converged when the shifts in parameters were less than 0·1 of the estimated deviations. The refined parameters are given in table 2. A list of F_0^2 and $|F_C|^2$ is shown in table 3. The final value of the extinction parameter G was 0·366 $\times 10^4$. This corresponds to an equivalent mosaic spread of 16 sec of arc in the sample crystal. The agreement factors between F_0^2 and $|F_C|^2$ were as follows:

| Number of reflections	1148	1022 $(F_0^2 > \sigma)$
$R(F^2) = \dfrac{\Sigma\, |F_0^2 - |F_C|^2|}{\Sigma\, F_0^2}$	0·068	0·063
$wR(F^2) = \left[\dfrac{\Sigma \omega\, |F_0^2 - |F_C|^2|^2}{\Sigma w F_0^4}\right]^{\frac{1}{2}}$	0·068	0·066

5. Discussion

5.1. *Comparison with the x-ray structure*

In the x-ray study of L_s-threonine, Shoemaker *et al* (1950) refined the positional parameters and a single isotropic temperature factor for the entire molecule. In order to make a quantitative comparison between the two sets of parameters from the two techniques, we carried out further refinement of the structure using 554 x-ray data listed as observed by Shoemaker *et al* (1950). The refinement procedure was similar to that described in section 4. Scattering factors for the hydrogens were those of Stewart *et al* (1965). The weighting scheme was derived from the error analysis to be

$$w^{-\frac{1}{2}} = 0.777 + 4.626 \times 10^{-2}\, F_0^2 + 1.017 \times 10^{-5}\, F_0^4 \tag{9}$$

In the isotropic refinement, the temperature factors of most of the hydrogen atoms became negative. These were then constrained to the anisotropic values obtained in our neutron study and an over all temperature factor to take into account any possible differences in the x-ray and neutron values of these was varied. The extinction correction factor G was also included. Upon convergence, the various agreement factors were: $R(F) = 0.038$ (compared to the value 0·112 reported by Shoemaker *et al* 1950), $R(F^2) = 0.061$ and $wR(F^2) = 0.107$. The refined x-ray parameters are also listed in table 1. Comparison between the two sets of positional parameters for heavy atoms shows a good agreement. Only three, $y(N)$, $y(O^{\gamma 1})$ and $z(C^\beta)$ have the weighted differences, $[= \Delta p_i/\sigma(p_i)]$, where $\sigma(p_i)$ is the pooled standard deviation $[=(\sigma^2 \text{ neutrons} + \sigma^2 \text{ x-rays})^{\frac{1}{2}}]$, greater than 2. The temperature factors β_{ii}'s for the heavy atoms in
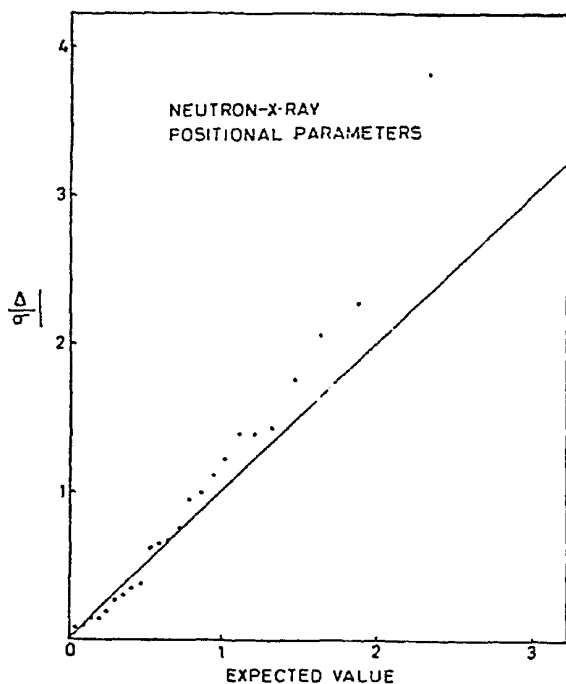
Figure 2. Half-normal probability plot comparison of positional parameters of non-hydrogen atoms in L_s–threonine.
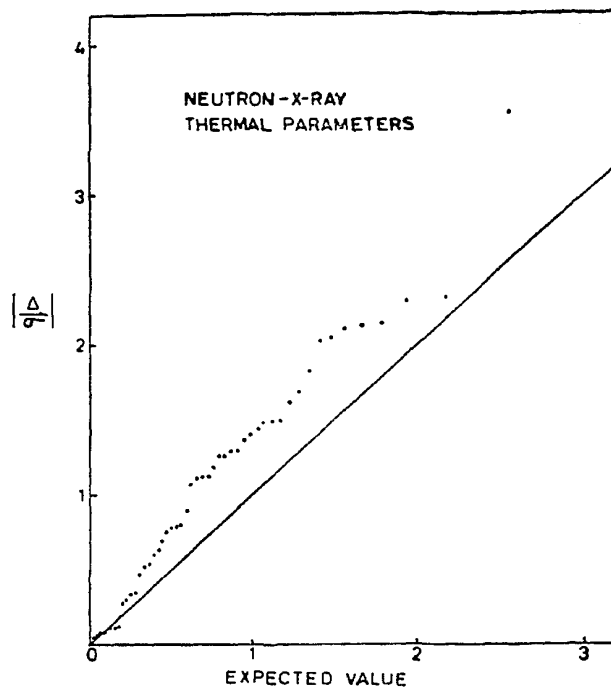
Figure 3. Half-normal probability plot comparison of anisotropic thermal parameters of non-hydrogen atoms in L_s–threonine.

the x-ray case are systematically larger than those from neutrons. The average difference between the two sets is equivalent to an isotropic ΔB of 0·77 $Å^2$. Such differences between x-ray and neutron temperature factors have also been noted in aminoacids, L–lysine·HCl·$2H_2O$ (Bugayong *et al* 1972) and L–cysteic acid·H_2O (Ramanadham *et al* 1973). ΔB for these structures is 0·91 $Å^2$ and 0·21 $Å^2$ respectively.

Further comparison was done by the half normal probability plot method (Abrahams and Keve 1971). These plots for the positional and temperature parameters differences for the heavy atoms are shown in figures 2 and 3. For the later, equivalent $\Delta\beta_{ii}$'s corresponding to ΔB=0·77 $Å^2$ were first subtracted from the x-ray β_{ii}'s. In both plots straight lines passing through the origin were obtained showing that the differences in the two sets are approximately normally distributed. The slopes of the two lines are 1·16 and 1·40. These correspond to an underestimation of the pooled $\sigma(p_i)$'s by the same factor.

5.2. *Molecular dimensions*

A stereo-view of a molecule of L_s–threonine is shown in figure 4. The bond distances and bond angles for the molecule computed from the final neutron and x-ray coordinates are given in tables 4 and 5. The molecular dimensions for the heavy atoms from the neutron and x-ray studies are nearly identical except for the $C^\beta - O^{\gamma 1}$ distance which differs by 4σ. The corresponding C—O distances in the structures of DL–serine, L–serine·H_2O (Frey *et al* 1973) and 4-hydroxy–L–proline (Koetzle *et al* 1973) are 1·403, 1·414 and 1·413 Å respectively, nearer to the neutron value. The $C^\beta - C^{\gamma 2}$ bond length reported to be abnormally short (1·505 Å) by Shoemaker *et al* (1950) has now been refined to 1·515 and 1·513 Å in the two refinements. The bond distances
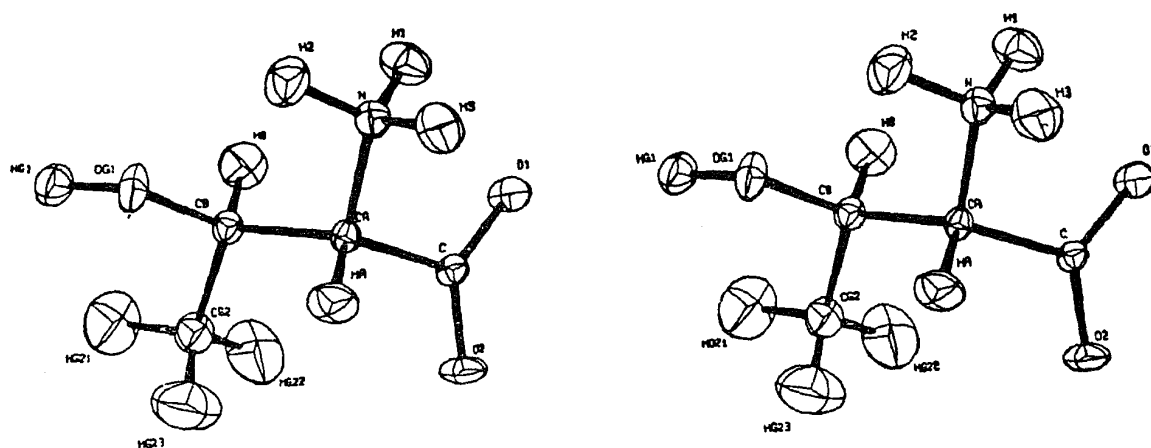
Figure 4. Stereoscopic picture of the molecule of L$_S$-threonine.
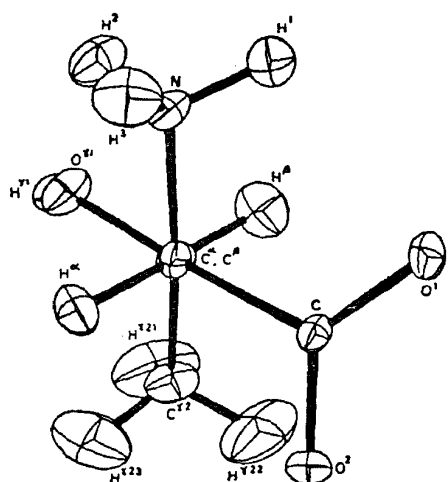

Figure 5. L$_S$-threonine molecule as seen when one looks down C$^\alpha$—C$^\beta$ bond.

and angles for the backbone atoms are compared in column 3 of tables 4 and 5 with the weighted average values from 14 aminoacids with ionised carboxylic group studied by neutron diffraction at Brookhaven and Trombay. The deviations are the largest for the distance C$^\alpha$—C$^\beta$ and the angle C—C$^\alpha$—C$^\beta$. The latter is due to considerable variations in the values of the angle C—C$^\alpha$—C$^\beta$ in different aminoacids and as Marsh and Donohue (1967) have noted may be the result of non-bonded contacts involving side chain atoms.

The threonine molecule exists as a zwitterion in the crystal with C$^\alpha$—NH$_3^+$ group nearly tetrahedral. The average dimensions of the NH$_3^+$ group are: $\langle$N$^+$—H$^i\rangle$ = 1·032 Å, angle $\langle$C$^\alpha$—N—H$^i\rangle$ = 110·1° and $\langle$H^i—N—H$^j\rangle$ = 108·8°. The corresponding weighted average values from other aminoacids are 1·039 Å, 110·6° and 108·5°.

The mean dimensions of the methyl group are: $\langle$C$^{\gamma 2}$—H$^{\gamma 2i}\rangle$ = 1·095 Å, $\langle$C$^\beta$—C$^{\gamma 2}$—H$^{\gamma 2i}\rangle$ = 110·9° and $\langle$H$^{\gamma 2i}$—C$^{\gamma 2}$—H$^{\gamma 2j}\rangle$ = 108·0°. It can be seen from figure 4 that the thermal motion ellipsoids for the CH$_3$ group atoms are larger than others. This is due to the librational motion of the methyl group about the C$^\beta$—C$^{\gamma 2}$ axis. A similar situation exists for the methyl group in the structure of L-alanine (Lehman *et al* 1972).

Table 4. Interatomic distance in L_S–threonine*

Bond Description	Neutron	X-ray	Weighted average values**
$C - O^1$	1·237(4) Å	1·243(4) Å	1·246 Å
$C - O^2$	1·258(4)	1·253(4)	1·255
$C^\alpha - C$	1·539(3)	1·537(4)	1·531
$C^\alpha - N$	1·490(3)	1·490(4)	1·487
$C^\alpha - C^\beta$	1·538(3)	1·532(4)	1·524
$C^\beta - O^{\gamma 1}$	1·416(4)	1·431(4)	
$C^\beta - C^{\gamma 2}$	1·515(5)	1·513(6)	
$N - H^1$	1·037(6)	0·98 (4)	
$N - H^2$	1·024(6)	0·90 (4)	
$N - H^3$	1·034(6)	0·91 (4)	
$C^\alpha - H^\alpha$	1·096(6)	0·96 (4)	1·096
$C^\beta - H^\beta$	1·107(7)	1·03 (4)	
$O^{\gamma 1} - H^{\gamma 1}$	0·983(6)	0·75 (4)	
$C^{\gamma 2} - H^{\gamma 21}$	1·097(9)	0·95 (5)	
$C^{\gamma 2} - H^{\gamma 22}$	1·075(10)	1·02 (5)	
$C^{\gamma 2} - H^{\gamma 23}$	1·113(10)	1·02 (5)	

*Parameters listed both in tables 4 and 5 are uncorrected for thermal motion. The standard deviations of the unit cell constants were also included in estimating the standard deviations of these parameters.

**The weighted average values defined as $\left\{ \left[\sum_i (x_i/\sigma_i^2) \right] / \left[\sum_i (1/\sigma_i^2) \right] \right\}$ are based on the neutron diffraction studies of 14 aminoacid structures studied at Brookhaven and Trombay.
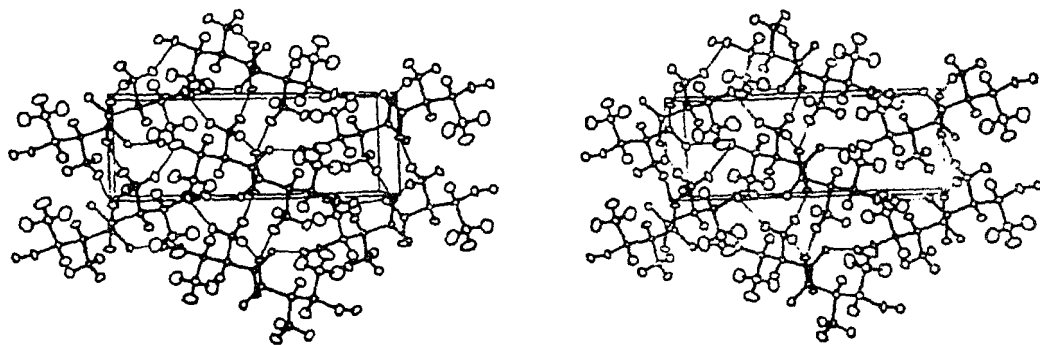
Table 5. Bond angles in L_S–threonine

Angle description	Neutron	X-ray	Weight average values*
$O^1 - C - C^\alpha$	116·3°(3)	116·5°(3)	117·6°
$O^2 - C - C^\alpha$	116·4(2)	116·3(3)	116·6
$O^2 - C - O^1$	127·2(3)	127·2(3)	125·7
$C - C^\alpha - N$	109·9(2)	110·0(2)	110·2
$C - C^\alpha - C^\beta$	112·6(2)	112·7(2)	110·9
$N - C^\alpha - C^\beta$	108·9(2)	108·8(2)	110·2
$C^\alpha - C^\beta - O^{\gamma 1}$	104·2(2)	104·2(2)	
$C^\alpha - C^\beta - C^{\gamma 2}$	113·1(2)	113·6(3)	
$O^{\gamma 1} - C^\beta - C^{\gamma 2}$	110·9(2)	112·2(3)	
$C^\alpha - N - H^1$	111·4(4)	108(2)	
$C^\alpha - N - H^2$	109·8(4)	116(2)	
$C^\alpha - N - H^3$	109·2(4)	107(3)	
$H^1 - N - H^2$	108·3(5)	105(3)	
$H^1 - N - H^3$	111·5(5)	116(3)	
$H^2 - N - H^3$	106·6(5)	106(3)	
$C - C^\alpha - H^\alpha$	109·8(4)	110(2)	108·6
$N - C^\alpha - H^\alpha$	107·1(4)	108(2)	107·6
$C^\beta - C^\alpha - H^\alpha$	108·4(4)	107(2)	108·8
$C^\alpha - C^\beta - H^\beta$	108·0(4)	111(2)	
$O^{\gamma 1} - C^\beta - H^\beta$	109·7(4)	111(2)	
$C^{\gamma 2} - C^\beta - H^\beta$	110·6(6)	106(2)	
$C^\beta - O^{\gamma 1} - H^{\gamma 1}$	112·6(4)	109(3)	
$C^\beta - C^{\gamma 2} - H^{\gamma 21}$	109·2(6)	109(3)	
$C^\beta - C^{\gamma 2} - H^{\gamma 22}$	112·0(6)	111(3)	
$C^\beta - C^{\gamma 2} - H^{\gamma 23}$	111·4(6)	113(3)	
$H^{\gamma 21} - C^{\gamma 2} - H^{\gamma 22}$	109·0(7)	105(4)	
$H^{\gamma 21} - C^{\gamma 2} - H^{\gamma 23}$	106·2(8)	113(4)	
$H^{\gamma 22} - C^{\gamma 2} - H^{\gamma 23}$	108·9(8)	106(4)	

*Based on the neutron diffraction studies of 14 aminoacid structures studied at Brookhaven and Trombay.

Table 6. Torsion angles in L_S-threonine

Angle	Description	Neutron	X-ray
ϕ^1	C —C$^\alpha$—N—H^1	46·4°(4)	48°(2)
ϕ^2	C —C$^\alpha$—N —H^2	166·4(4)	165(3)
ϕ^3	C —C$^\alpha$—N —H^3	−77·1(4)	−77(2)
ψ^1	N —C$^\alpha$—C —O^1	−25·8(3)	−25·6(4)
ψ^2	N —C$^\alpha$—C —O^2	155·3(3)	155·8(3)
$\chi^{1,1}$	N —C$^\alpha$—C$^\beta$—O$^{\gamma_1}$	−55·1(3)	−54·8(3)
$\chi^{1,2}$	N —C$^\alpha$—C$^\beta$—C$^{\gamma_2}$	−175·8(2)	−175·9(3)
$\chi^{1,3}$	N —C$^\alpha$—C$^\beta$—H$^\beta$	61·5(4)	64(2)
$\chi^{2,1}$	C$^\alpha$—C$^\beta$—O$^{\gamma_1}$—H$^{\gamma_1}$	−175·8(5)	−177(3)
$\chi^{2,2,1}$	C$^\alpha$—C$^\beta$—C$^{\gamma_2}$—H$^{\gamma_2}{}_{,1}$	52·8(6)	58(3)
$\chi^{2,2,2}$	C$^\alpha$—C$^\beta$—C$^{\gamma_2}$—H$^{\gamma_2}{}_{,2}$	173·7(6)	173(3)
$\chi^{2,2,3}$	C$^\alpha$—C$^\beta$—C$^{\gamma_2}$—H$^{\gamma_2}{}_{,3}$	−64·1(6)	−68(4)

Figure 6. Stereoscopic picture of molecular packing and hydrogen bonding in the unit cell of L_S–threonine crystal.

5.3. *The molecular conformation*

The conformation of the molecule is shown in figure 5 and the torsion angles are given in table 6. The torsion angle labelling is in accordance with the IUPAC–IUB commission on Biochemical Nomenclature (1970). The staggered ethane-type conformation of the threonine molecule about the C$^\alpha$—C$^\beta$ bond found by Shoemaker *et al* (1950) is confirmed. The hydrogens of the NH$_3^+$ group (angles ϕ^1, ϕ^2 and ϕ^3) are rotated about C$^\alpha$—N by about 14° in the counter-clockwise direction from the ideal staggered configuration with respect to the substituents on the C$^\alpha$ atom. This departure from the ideal position appears to be due to the influence of hydrogen bonding. The difference between the angles ψ^1 and ψ^2 of 181° shows that the group C$^\alpha$—C—(O^1, O^2) is planar. The values ± 25° for these torsion angles show that the nitrogen atom is significantly displaced from this plane. The methyl group is also in the staggered conformation with reference to the groups on the C$^\beta$ atom.

5.4. *Molecular packing and hydrogen bonding*

The hydrogen bonding scheme in the crystal is depicted in the stereo drawing (figure 6) of the packing of the molecules in the unit cell. There are four hydrogen bonds per molecule — three from the NH$_3^+$ group and one from the O—H group. The hydrogen bond N—H^1—O^2 links the threonine molecules to form chains along the c-axis of the crystal. The other three hydrogen bonds bind these chains together in a three dimensional network. All the hydrogen bond distances and angles are sum-

Table 7. Hydrogen bonding in L_S–Threonine

X—H⋯Y		X—H	H⋯Y	X⋯Y	H—X⋯Y
N—H¹...O²	(I)	1·037(6)Å	1·900(7)Å	2·917(4)Å	9·0°(3)
N—H²...O⁷¹	(II)	1·024(6)	2·202(7)	3·124(4)	21·2(3)
N—H³...O²	(IV)	1·034(6)	1·791(7)	2·794(4)	11·0(4)
O⁷¹—H⁷¹...O¹	(III)	0·983(6)	1·716(6)	2·660(4)	13·0(3)

Symmetry code for the acceptor atom:

(I)	x	y	$1+z$	
(II)	$\frac{1}{2}-x$	$-y$	$\frac{1}{2}+z$	
(III)	$-\frac{1}{4}+x$	$\frac{1}{2}-y$	$1-z$	
(IV)	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	

marized in table 7. Apart from a hydrogen bond to $O^{\gamma 1}$ (II), the atom H^2 has a short intramolecular contact $H^2-O^{\gamma 1}$ of 2·214 Å. The $N-H^2-O^{\gamma 1}$ angle is 107·0°. Because of this unfavourable angle, we do not classify this as a bifurcated hydrogen bond system although the weak interaction present may explain why the $N-H^2-O^{\gamma 1}$ (II) bond is found to be the most bent as well as the longest $N-H\cdots O$ hydrogen bond in the structure.

6. Computer programs used

The computations described in this paper were done on the CDC 3600 and BESM–6 computers. The following programs were used.

No.	*Program name*	*Purpose*	*Reference*
1.	REFINE	Setting angles and least squares refinement of cell parameters	Srikanta and Sequeira 1968
2.	DATARED	Data reduction (absorption correction included as a subroutine)	Srikanta 1968
3.	FORDAP	Fourier calculations	Zalkin 1962
4.	TANFMULA	Tangent formula calculation of phases	Sikka 1970
5.	XFLS	Least squares program for structure refinement	Busing *et al* 1962*
6.	ORFFE	Bond distances and angles	Busing *et al* 1964*
7.	ORTEP	Stereo plotting	Johnson 1965†
8.	TORANG	Torsion angles	Ramanadham 1970

*The BESM–6 version by H Rajagopal

†The CDC 3600 version by H Rajagopal and A Sequeira

Acknowledgements

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