ACTA CHEMICA SCANDINAVICA 26 (1972) 3819–3833

Crystal Structure of L-Tyrosine

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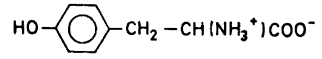
The crystal structure of L-tyrosine has been determined by X-ray methods using 2259 unique reflections collected by counter diffractometer techniques. The unit cell is orthorhombic, space group $P2_12_12_1$, with dimensions $a=6.91_3$ Å, $b=21.11_6$ Å, $c=5.82_9$ Å, and contains four molecules. The structure was solved by direct methods and refined to a conventional R factor of 0.049 by least-squares methods. Estimated standard deviations in bond lengths not involving hydrogen atoms are 0.002 Å and in angles 0.1 – 0.2°. The conformation about the C7 – C8 bond is staggered with the C8 hydrogen atom *anti* relative to the phenyl ring. The crystal structure is stabilized through a three-dimensional network of hydrogen bonds.

L-Tyrosine plays an important role in the living organism, not only as a building unit in proteins but also by taking part in the biosynthesis of



hormones, neurotransmitters, and pigments. During the last 20 years several papers on the structure of salts and derivatives of this compound have been published as contributions to the physical characterization of the molecule. Crystal structure data on L-tyrosine itself have been lacking, however, presumably because of the difficulty of obtaining crystals suitable for X-ray examination. In the course of the structure investigation of several biologically important amino acids a method of growing single crystals of L-tyrosine has been found. The crystallization procedure as well as a brief description of the result of the X-ray crystal structure analysis have been published elsewhere.[1,2] In the present report we are presenting a more detailed account of the structure determination and a discussion of the crystal and molecular structure of this amino acid.

EXPERIMENTAL

Commercially obtained L-tyrosine was recrystallized according to the method given in Ref. 1. A single crystal of dimensions $0.3 \times 0.4 \times 0.7$ mm^3 was used in all X-ray experiments; it was mounted with the direction of the largest dimension, the crystallographic c axis, along the goniometer axis.

Oscillation and Weissenberg photographs indicated orthorhombic symmetry. The extinctions uniquely determined the space group to be $P2_12_12_1$ in agreement with the result obtained by Boggs and Donohue.[3] Unit cell dimensions were determined from diffractometer measurements on five general reflections and their Laue-symmetric equivalents. A manual Picker diffractometer was applied using Cu$K\beta$ radiation (λ = 1.3922 Å) and a take-off angle of 0.5°. The computer program used in the least-squares calculations of cell parameters, as well as the programs employed during the subsequent calculations are parts of an assembly of programs for a CD-3300 computer and described in Ref. 4.

Three-dimensional intensity data were recorded with the use of an automatic Picker four-angle diffractometer using graphite crystal monochromated MoK radiation. The take-off angle was 4° and the temperature was kept constant to within 1° at 18°C. Diffraction data for 2948 reflections with $2\theta < 80°$ were measured using the $\omega - 2\theta$ scanning mode with a 2θ scan speed of 2° min^{-1} through the scan range from 0.55° below $2\theta(\alpha_1)$ to 0.65° above $2\theta(\alpha_2)$. Background counts were taken for 20 sec at each of the scan range limits. Three standard reflections measured after every 100 reflections showed no significant fluctuation during the experiment. The 2259 reflections greater than $2\sigma(I)$ were considered to be observed; the remaining 689 reflections were excluded from the structure refinement procedure. Lorentz and polarization corrections were applied to the intensity data.

Atomic form factors used were those of Hanson *et al.*[5] for oxygen, nitrogen, and carbon, and of Stewart *et al.*[6] for hydrogen.

CRYSTAL DATA

L-4-Hydroxyphenylalanine (L-tyrosine) $C_9H_{11}O_3N$, orthorhombic. a = 6.913 (0.005) Å; b = 21.116 (0.003) Å; c = 5.829 (0.004) Å. Figures in parentheses are estimated standard deviations. V = 850.9 Å^3; M = 181.19; $F(000)$ = 384; (Z = 4. D_{obs} (flotation) = 1.41 g cm^{-3}, D_{calc} = 1.414 g cm^{-3}. Absent reflections: ($h00$) for h odd, ($0k0$) for k odd, ($00l$) for l odd; space group $P2_12_12_1$.

DETERMINATION OF THE STRUCTURE

The phases of 400 normalized structure amplitudes were obtained by the application of the symbolic addition procedure and the tangent formula.[7,8] Three-dimensional F-maps were calculated with eight sets of phases for the 400 structure factors and in one of the maps the 13 largest peaks were consistent with the non-hydrogen atoms of a reasonable model for the L-tyrosine molecule.

Preliminary refinements were carried out by the minimum residual method [9] followed by three cycles of least squares refinement. At this stage stereochemically reasonable hydrogen atomic positions were postulated and anisotropic thermal parameters for non-hydrogen atoms introduced. Several full-matrix least-squares refinement cycles were calculated resulting in a conventional R value of 0.049 and a weighted R of 0.046. The overdetermination ratio was 13.9, 162 parameters being refined on the basis of 2259 reflections with $\sin\theta/\lambda < 0.9$ Å^{-1}.

A comparison of observed and calculated structure factors is given in Table 1; the final parameters for non-hydrogen atoms are listed in Table 2, and for hydrogen atoms in Table 3.

Magnitudes and directions of the principal axes of the ellipsoids of vibration are given in Table 4. An analysis of the thermal parameters showed that the phenol and alanine parts may be regarded separately as rigid bodies

Table 1. Observed and calculated structure factors. The columns are *h*, *k*, *l*, 10 F_o and 10 F_c.

0	4	0	291	291
0	6	0	356	349
0	8	0	581	583
0	10	0	598	592
0	12	0	104	97
0	14	0	59	55
0	16	0	99	99
0	18	0	125	136
0	20	0	219	226
0	22	0	57	50
0	24	0	78	78
0	26	0	44	40
0	28	0	25	31
1	29	0	22	22
1	28	0	51	49
1	27	0	51	45
1	26	0	41	41
1	25	0	50	55
1	23	0	48	48
1	20	0	124	130
1	19	0	49	44
1	18	0	24	22
1	17	0	107	107
1	16	0	131	127
1	15	0	94	92
1	14	0	199	191
1	13	0	203	203
1	12	0	324	320
1	11	0	46	49
1	10	0	213	204
1	9	0	49	48
1	8	0	380	367
1	7	0	312	315
1	6	0	473	464
1	5	0	698	711
1	4	0	308	314
1	3	0	689	705
1	2	0	369	371
1	1	0	216	221
2	0	0	826	836
2	1	0	53	53
2	2	0	711	740
2	3	0	564	565
2	4	0	109	103
2	5	0	302	289
2	6	0	374	378
2	7	0	96	92
2	8	0	228	230
2	9	0	132	129
2	10	0	89	86
2	11	0	354	347
2	12	0	69	68
2	13	0	390	391
2	14	0	19	20
2	15	0	13	12
2	16	0	172	177
2	17	0	54	56
2	18	0	156	162
2	19	0	142	142
2	20	0	67	70
2	21	0	14	13
2	22	0	67	70
2	23	0	24	26
2	24	0	32	35
2	25	0	22	22
2	26	0	94	92
2	28	0	66	67
3	27	0	26	17
3	26	0	44	41
3	25	0	68	60
3	24	0	70	66
3	23	0	58	61
3	22	0	48	49
3	21	0	53	51
3	20	0	87	90
3	19	0	67	64
3	18	0	48	45
3	17	0	66	71
3	16	0	83	81
3	14	0	88	86
3	13	0	52	48
3	12	0	200	199
3	11	0	231	239
3	10	0	162	159
3	9	0	226	231
3	8	0	156	155
3	7	0	170	170
3	6	0	71	64
3	5	0	79	68
3	4	0	147	147
3	3	0	96	99
3	2	0	9	11
3	1	0	84	82
4	0	0	35	31
4	1	0	89	89
4	2	0	149	148
4	3	0	253	250
4	4	0	83	84
4	5	0	23	26
4	6	0	149	151
4	7	0	89	87
4	8	0	19	19
4	9	0	28	28
4	10	0	68	70
4	11	0	43	40
4	12	0	77	81
4	13	0	197	203
4	14	0	176	176
4	15	0	25	18
4	16	0	55	55
4	17	0	90	88
4	18	0	92	93
4	19	0	40	38
4	20	0	78	78
4	21	0	32	26
4	22	0	75	76
4	23	0	68	70
4	24	0	58	55
4	25	0	19	23
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5	23	0	33	33
5	22	0	76	73
5	21	0	23	22
5	20	0	79	77
5	18	0	89	91
5	16	0	29	27
5	15	0	103	106
5	14	0	49	50
5	13	0	84	83
5	12	0	33	30
5	11	0	101	105
5	9	0	89	94
5	8	0	16	15
5	7	0	145	147
5	6	0	114	114
5	5	0	38	38
5	4	0	23	30
5	3	0	100	99
5	2	0	234	238
5	1	0	31	33
6	0	0	117	118
6	1	0	43	40
6	2	0	22	21
6	3	0	39	39
6	4	0	139	141
6	5	0	58	59
6	6	0	43	42
6	7	0	69	67
6	8	0	15	15
6	9	0	27	28
6	10	0	93	97
6	11	0	87	86
6	12	0	18	18
6	13	0	126	126
6	14	0	197	196
6	15	0	72	74
6	16	0	80	80
6	17	0	33	36
6	18	0	63	63
6	19	0	60	58
6	20	0	33	29
6	22	0	35	35
7	20	0	27	21
7	18	0	68	64
7	17	0	85	84
7	16	0	65	64
7	14	0	38	35
7	13	0	33	33
7	12	0	16	13
7	9	0	116	117
7	7	0	25	27
7	6	0	58	64
7	3	0	33	33
7	2	0	133	131
7	1	0	90	92
8	0	0	83	86
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8	4	0	19	17
8	5	0	29	27
8	6	0	70	67
8	7	0	58	57
8	8	0	28	28
8	9	0	23	19
8	10	0	29	33
8	11	0	61	61
8	12	0	69	89
8	13	0	55	57
8	14	0	53	51
8	15	0	47	43
8	16	0	24	26
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9	4	0	27	25
9	2	0	36	35
9	1	0	49	46
9	0	1	33	35
9	1	1	54	51
9	2	1	37	38
9	3	1	30	28
9	4	1	30	27
9	5	1	19	16
9	7	1	51	50
9	8	1	31	29
9	9	1	35	32
8	15	1	41	34
8	14	1	28	28
8	13	1	49	48
8	12	1	31	31
8	11	1	47	45
8	10	1	26	27
8	9	1	72	71
8	8	1	39	39
8	7	1	41	41
8	6	1	58	53
8	4	1	81	79
8	3	1	40	38
8	2	1	47	46
8	1	1	49	50
8	0	1	22	18
7	0	1	15	14
7	1	1	112	112
7	2	1	26	26
7	3	1	38	39
7	4	1	70	67
7	5	1	47	48
7	6	1	40	37
7	7	1	38	38
7	9	1	99	97
7	10	1	53	51
7	11	1	87	87
7	12	1	58	57
7	13	1	76	73
7	14	1	29	28
7	15	1	50	54
7	17	1	52	54
7	18	1	69	67
7	19	1	57	54
6	20	1	38	36
6	19	1	16	12
6	18	1	65	67
6	17	1	85	83
6	16	1	37	33
6	15	1	34	35
6	14	1	45	44
6	13	1	22	25
6	12	1	65	69
6	11	1	40	45
6	10	1	89	88
6	9	1	54	52
6	8	1	62	63
6	7	1	74	77
6	6	1	39	40
6	5	1	108	107
6	4	1	135	135
6	3	1	173	171
6	2	1	115	117
6	1	1	21	17
6	0	1	13	8
5	0	1	39	35
5	1	1	28	28
5	2	1	224	228
5	3	1	31	27
5	4	1	28	26
5	5	1	63	65
5	6	1	99	101
5	7	1	137	138
5	8	1	33	33
5	9	1	71	69
5	10	1	80	85
5	11	1	48	48
5	12	1	63	62
5	13	1	147	149
5	14	1	23	25
5	15	1	171	171
5	16	1	30	37
5	17	1	98	98
5	18	1	61	63
5	19	1	54	58
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5	21	1	77	77
5	22	1	51	44
5	24	1	20	17
4	26	1	31	36
4	25	1	29	27
4	23	1	65	66
4	22	1	64	65
4	21	1	108	109
4	20	1	44	42
4	19	1	26	31
4	18	1	39	35
4	17	1	78	77
4	16	1	106	109
4	15	1	212	220
4	14	1	105	105
4	13	1	57	60
4	12	1	26	31
4	11	1	66	67
4	10	1	106	106
4	9	1	87	87
4	8	1	59	56
4	7	1	118	116
4	6	1	75	75
4	5	1	124	123
4	4	1	109	109
4	3	1	337	336
4	2	1	175	171
4	1	1	263	263
4	0	1	125	121
3	0	1	206	210
3	1	1	397	395
3	2	1	280	278
3	3	1	120	118
3	4	1	275	274
3	5	1	205	203
3	6	1	164	166
3	7	1	134	133
3	8	1	35	39
3	9	1	69	70
3	10	1	118	121
3	11	1	162	163
3	12	1	69	70
3	13	1	109	118
3	14	1	76	79

Table 1. Continued.

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3	16	1	53	56	0	23	1	60	54	1	2	2	493	468	4	16	2	198	201	8	3	2	53	53
3	17	1	51	56	0	22	1	57	56	1	1	2	293	258	4	17	2	31	30	8	4	2	50	54
3	18	1	63	63	0	21	1	61	65	1	0	2	366	342	4	18	2	56	55	8	5	2	54	59
3	19	1	38	39	0	20	1	48	48	2	0	2	57	63	4	19	2	43	44	8	6	2	67	69
3	20	1	75	76	0	19	1	105	113	2	1	2	220	211	4	22	2	49	48	8	7	2	27	31
3	22	1	40	39	0	18	1	76	81	2	2	2	124	113	4	23	2	29	27	8	8	2	82	80
3	23	1	64	62	0	17	1	109	108	2	3	2	453	439	4	24	2	49	47	8	9	2	22	15
3	24	1	57	55	0	16	1	19	26	2	4	2	213	205	4	25	2	24	22	8	10	2	21	20
3	25	1	35	30	0	15	1	54	61	2	5	2	232	223	5	23	2	41	40	8	12	2	20	27
3	26	1	29	29	0	14	1	131	132	2	6	2	168	162	5	22	2	38	37	8	13	2	27	22
3	27	1	36	35	0	13	1	21	22	2	7	2	154	156	5	21	2	21	19	8	14	2	51	47
2	28	1	57	52	0	11	1	228	223	2	8	2	42	41	5	20	2	30	29	9	6	2	33	31
2	27	1	24	23	0	10	1	230	222	2	9	2	74	73	5	19	2	73	77	9	4	2	21	22
2	26	1	28	27	0	9	1	147	141	2	10	2	99	101	5	18	2	25	22	9	3	2	65	64
2	25	1	29	30	0	8	1	35	41	2	11	2	114	114	5	17	2	40	39	9	2	2	30	28
2	24	1	34	33	0	7	1	275	263	2	12	2	70	74	5	16	2	20	23	9	1	2	27	29
2	21	1	22	26	0	6	1	60	48	2	13	2	212	218	5	15	2	131	132	9	0	2	52	49
2	20	1	57	52	0	5	1	230	220	2	14	2	144	146	5	13	2	36	36	8	10	3	55	56
2	19	1	61	65	0	3	1	255	252	2	15	2	148	155	5	12	2	38	35	8	9	3	32	29
2	18	1	138	141	0	2	1	140	148	2	16	2	46	46	5	11	2	128	132	8	8	3	44	44
2	17	1	146	149	0	1	1	339	294	2	17	2	173	179	5	9	2	50	50	8	7	3	67	66
2	16	1	129	134	0	0	2	408	336	2	18	2	97	101	5	8	2	31	30	8	6	3	59	60
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2	13	1	111	112	0	3	2	50	35	2	23	2	20	19	5	5	2	188	186	8	2	3	20	24
2	12	1	250	253	0	4	2	332	320	2	24	2	36	34	5	4	2	219	226	8	1	3	55	54
2	11	1	104	100	0	5	2	407	402	2	25	2	41	42	5	3	2	65	67	8	0	3	89	89
2	10	1	275	267	0	6	2	313	305	2	26	2	44	41	5	2	2	69	67	7	0	3	100	101
2	9	1	62	59	0	7	2	128	123	2	27	2	70	68	5	1	2	108	107	7	1	3	86	84
2	8	1	121	121	0	8	2	78	84	3	26	2	48	44	5	0	2	19	16	7	2	3	130	130
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2	0	1	331	318	0	17	2	235	240	3	18	2	86	89	6	7	2	34	39	7	10	3	22	18
1	0	1	587	553	0	18	2	72	73	3	17	2	135	137	6	8	2	50	52	7	11	3	41	39
1	1	1	694	671	0	21	2	52	53	3	16	2	101	105	6	9	2	56	59	7	12	3	85	83
1	2	1	337	319	0	22	2	28	29	3	15	2	135	130	6	10	2	85	86	7	14	3	26	22
1	3	1	56	51	0	23	2	74	74	3	14	2	123	129	6	11	2	15	6	7	15	3	42	47
1	4	1	402	391	0	24	2	54	53	3	13	2	110	112	6	12	2	43	45	7	16	3	21	20
1	5	1	249	239	0	25	2	41	43	3	12	2	118	122	6	13	2	27	33	6	20	3	50	45
1	6	1	123	117	0	26	2	36	32	3	10	2	174	178	6	14	2	32	34	6	19	3	31	36
1	7	1	188	184	0	27	2	26	32	3	9	2	176	176	6	15	2	44	41	6	18	3	78	75
1	8	1	143	138	0	28	2	66	64	3	8	2	98	99	6	16	2	66	64	6	17	3	21	17
1	9	1	272	266	1	28	2	103	100	3	7	2	183	180	6	17	2	54	54	6	16	3	30	30
1	10	1	127	125	1	26	2	31	33	3	6	2	110	102	6	18	2	47	41	6	15	3	47	44
1	11	1	218	213	1	25	2	105	101	3	5	2	140	141	6	19	2	34	33	6	14	3	26	25
1	12	1	185	183	1	24	2	36	34	3	4	2	211	206	6	20	2	42	37	6	12	3	61	66
1	13	1	174	177	1	23	2	54	52	3	3	2	228	222	6	21	2	59	57	6	11	3	31	33
1	14	1	179	181	1	22	2	44	42	3	2	2	292	286	7	18	2	29	29	6	10	3	80	80
1	15	1	80	83	1	20	2	21	25	3	1	2	145	139	7	17	2	47	44	6	9	3	64	63
1	16	1	55	59	1	19	2	24	28	3	0	2	229	224	7	16	2	24	20	6	8	3	15	24
1	17	1	140	141	1	18	2	213	219	4	0	2	36	39	7	15	2	21	18	6	7	3	29	30
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3	22	8	44	43	4	19	8	38	36	7	3	8	42	40	3	13	9	43	38	0	4	9	42	37
3	21	8	44	46	4	20	8	22	26	7	1	8	22	30	2	18	9	39	34	0	2	9	35	36
3	20	8	22	15	5	18	8	23	18	6	1	9	50	47	2	17	9	22	24	0	0	10	22	26
3	17	8	28	27	5	15	8	24	24	5	1	9	30	29	2	16	9	35	33	0	4	10	28	30
3	16	8	21	24	5	14	8	20	12	5	2	9	25	26	2	14	9	20	19	0	5	10	21	21
3	15	8	30	34	5	13	8	29	27	5	3	9	26	27	2	12	9	35	38	0	6	10	71	71
3	14	8	50	53	5	11	8	23	19	5	4	9	61	60	2	9	9	46	42	0	7	10	85	85
3	11	8	29	24	5	10	8	25	23	5	5	9	40	34	2	8	9	61	60	0	9	10	36	35
3	10	8	27	32	5	8	8	35	33	5	7	9	34	33	2	6	9	48	48	0	10	10	23	15
3	9	8	29	27	5	7	8	29	32	5	9	9	41	37	2	5	9	44	35	1	8	10	36	41
3	8	8	35	34	5	5	8	26	22	5	11	9	23	24	2	4	9	41	44	1	7	10	50	53
3	7	8	52	51	5	4	8	32	37	4	14	9	43	47	2	3	9	68	65	1	5	10	53	52
3	5	8	67	68	5	1	8	41	41	4	10	9	57	61	2	2	9	23	15	1	3	10	30	25
3	4	8	21	25	5	0	8	25	28	4	8	9	40	46	2	1	9	30	35	1	2	10	24	23
3	3	8	74	76	6	0	8	26	27	4	6	9	48	48	1	0	9	24	28	1	1	10	38	38
3	2	8	21	19	6	1	8	30	30	4	5	9	32	32	1	1	9	50	44	2	0	10	30	33
3	1	8	40	39	6	2	8	42	38	4	4	9	67	64	1	2	9	37	35	2	2	10	42	42
3	0	8	42	42	6	3	8	60	57	4	0	9	36	35	1	4	9	20	20	2	3	10	41	43
4	0	8	69	69	6	4	8	46	42	3	0	9	32	33	1	6	9	34	26	2	4	10	35	42
4	1	8	33	32	6	5	8	44	45	3	1	9	31	32	1	9	9	21	19	2	6	10	34	35
4	2	8	54	52	6	7	8	37	39	3	2	9	24	23	1	10	9	88	90	2	7	10	41	43
4	3	8	35	34	6	8	8	55	57	3	3	9	54	55	1	12	9	32	30	2	8	10	30	34
4	4	8	39	40	6	11	8	28	20	3	4	9	49	49	1	15	9	32	29	3	5	10	73	77
4	5	8	47	49	6	12	8	41	38	3	5	9	43	48	0	18	9	23	12	3	4	10	23	18
4	6	8	47	44	6	13	8	24	22	3	6	9	41	39	0	16	9	29	31	3	3	10	25	25
4	7	8	32	31	6	14	8	23	16	3	7	9	44	42	0	13	9	23	28	3	2	10	46	48
4	8	8	51	49	6	15	8	23	20	3	8	9	41	42	0	11	9	32	30	3	0	10	23	21
4	10	8	29	28	7	11	8	31	26															

Table 2. Fractional atomic coordinates and thermal parameters with estimated standard deviations ($\times 10^5$) for non-hydrogen atoms. The temperature factor is given by exp $-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O1	48 139	59 909	47 104	1973	113	1492	155	−303	3
O1	19	5	19	30	2	31	14	54	14
O2	16 646	33 312	62 615	1491	156	1469	116	533	−155
	17	5	20	24	2	30	14	53	16
O3	42 813	28 568	77 069	1830	173	879	87	−205	44
	19	5	18	28	3	26	15	50	14
N	24 134	30 395	19 616	1352	109	910	−3	−104	39
	20	5	20	26	2	28	14	50	15
C1	54 146	40 561	35 382	905	104	1116	−63	119	60
	21	6	24	26	2	34	14	54	16
C2	59 675	43 336	56 092	1145	123	1044	−19	−299	103
	23	6	25	29	3	33	16	58	17

Table 2. Continued.

C3	57 417	49 774	59 840	1214	123	916	−73	−273	−25
	24	6	25	29	3	33	16	56	16
C4	49 410	53 547	42 897	930	104	1191	6	126	41
	21	6	25	26	3	34	14	57	17
C5	43 388	50 888	22 293	1154	126	1182	3	−448	147
	24	7	26	30	3	36	16	61	17
C6	45 900	44 421	18 657	1181	131	1024	−101	−301	19
	23	7	25	29	3	33	16	55	17
C7	57 507	33 558	31 222	1127	109	1322	64	298	−18
	23	7	26	28	3	35	15	60	17
C8	40 003	29 337	36 562	1164	87	838	48	−44	−20
	21	6	23	28	2	29	14	54	15
C9	32 403	30 518	60 854	1339	81	904	−119	282	−69
	24	6	24	29	2	31	15	53	15

Table 3. Fractional atomic coordinates ($\times 10^4$) and isotopic thermal parameters (Å^2) with estimated standard deviations for hydrogen atoms.

Atom	*x*	*y*	*z*	*B*
H2	6559	4068	6705	1.88
	29	10	39	0.38
H3	6100	5177	7350	2.05
	30	10	38	0.40
H5	3758	5355	1090	1.96
	28	9	37	0.36
H6	4211	4255	316	2.60
	34	10	38	0.43
H71	6815	3207	4028	2.01
	28	8	38	0.37
H72	6143	3279	1442	3.21
	32	11	45	0.48
H8	4392	2501	3462	0.59
	23	7	27	0.26
HO1	4423	6154	3819	3.71
	44	12	55	0.66
HN1	1976	3415	1934	1.33
	28	10	39	0.39
HN2	1445	2780	2227	1.94
	28	9	37	0.38
HN3	2981	3002	542	2.89
	31	10	43	0.44

rather than the molecule as a whole. The phenol part has the axis of the largest oscillation amplitude nearly parallel to the C7 – C1 – C4 – O1 direction whereas the corresponding axis of the alanine moiety is roughly perpendicular to the C1 – C7 – C8 plane. The bond lengths were corrected for librational effects according to this model.

Standard deviations were calculated from the correlation matrix ignoring the standard deviations in cell parameters.

Table 4. R.m.s. amplitudes of vibration $(\bar{u}^2)^{\frac{1}{2}}$ (Å) and B-values (Å^2) along the principal axes of vibration given by the components of a unit vector **e** in fractional coordinates ($\times 10^3$).

Atom	$(\bar{u}^2)^{\frac{1}{2}}$	B	e_x	e_y	e_z
O1	.223	3.91	215	51	−428
	.160	2.03	0	77	141
	.154	1.88	040	−131	72
O2	.200	3.16	158	121	19
	.190	2.85	89	−132	104
	.143	1.61	−57	56	119
O3	.214	3.62	194	90	−92
	.194	2.98	80	176	18
	.122	1.17	−10	−81	121
N	.181	2.59	81	4	12
	.157	1.96	5	156	20
	.124	1.22	8	−16	123
C1	.159	2.00	−82	134	25
	.148	1.72	108	50	87
	.132	1.39	59	55	−105
C2	.173	2.37	−114	116	60
	.164	1.13	118	115	1
	.128	2.29	30	−32	120
C3	.178	2.49	−147	98	21
	.162	2.07	85	134	−33
	.123	1.19	26	13	120
C4	.156	1.91	65	126	66
	.151	1.79	125	−79	28
	.140	1.55	52	38	−124
C5	.178	2.51	−101	118	88
	.168	2.23	124	112	−07
	.129	1.32	46	−44	112
C6	.182	2.62	−125	130	29
	.160	2.03	109	113	−34
	.130	1.33	34	4	125

Table 4. Continued.

	.172	2.33	148	63	61
C7	.157	1.94	23	−132	81
	.143	1.62	−70	57	111
	.169	2.25	166	34	−7
C8	.139	1.53	28	−135	15
	.120	1.13	2	13	119
	.185	2.71	175	−53	33
C9	.133	1.39	44	112	−56
	.120	1.13	−4	54	107

DISCUSSION

A drawing of the molecule is shown in Fig. 1 in which the numbering of the atoms is indicated. The bond lengths (corrected) and valence angles are given in this figure, as well as in Table 5 in which the estimated standard deviations are also listed. The results presented are confirmed by a neutron diffraction study of the compound.[10]

In the alanine moiety the usual zwitterionic nature of a free amino acid is indicated both by the nearly equal carbon-oxygen bond length in the carboxyl group and the tetrahedral arrangement of hydrogen atoms around the nitrogen atom. The conformation about the N−C8 bond is staggered.

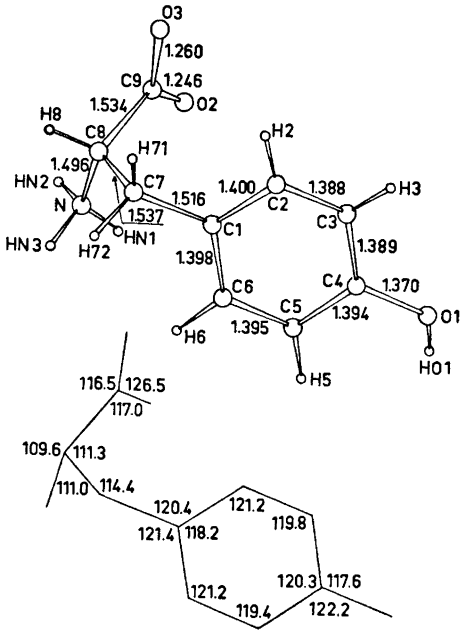

Fig. 1. Bond lengths (Å) corrected for thermal vibration effects and angles (°) in L-tyrosine.

Table 5. Bond lengths (Å) and bond angles (°). Estimated standard deviations (in parentheses) apply to the least significant digits.

Bond length		Corrected		Bond angle
C1–C2	1.395(2)	1.400	C1–C2–C3	121.2(1)
C2–C3	1.386(2)	1.388	C2–C3–C4	119.8(1)
C3–C4	1.384(2)	1.389	C3–C4–C5	120.3(1)
C4–C5	1.390(2)	1.394	C4–C5–C6	119.4(1)
C5–C6	1.393(2)	1.395	C1–C6–C5	121.2(1)
C1–C6	1.393(2)	1.398	C2–C1–C6	118.2(1)
C1–C7	1.516(2)		C7–C1–C2	120.4(1)
C7–C8	1.535(2)	1.537	C7–C1–C6	121.4(1)
C8–C9	1.531(2)	1.534	O1–C4–C5	122.2(1)
C8–N1	1.493(2)	1.496	O1–C4–C3	117.6(1)
C9–O2	1.243(2)	1.246	C1–C7–C8	114.4(1)
C9–O3	1.257(2)	1.260	C7–C8–C9	111.3(1)
C4–O1	1.369(2)	1.370	C7–C8–N1	111.0(1)
O1–HO1	0.68		N1–C8–C9	109.6(1)
N1–HN1	0.85		C8–C9–O2	117.0(1)
N1–HN2	0.88		C8–C9–O3	116.5(1)
N1–HN3	0.92		O2–C9–O3	126.5(1)
C2–H2	0.94			
C3–H3	0.93	Hydrogen bond lengths		
C5–H5	0.96	O1–O2($\frac{1}{2}-x$, $-y$, $\frac{1}{2}+z$)		2.671(2)
C6–H6	1.02	N –O1($\frac{1}{2}-x$, $-y$, $\frac{1}{2}+z$)		2.878(2(
C7–H71	0.96	N –O3($\frac{1}{2}+x$, $\frac{1}{2}-y$, $-z$)		2.882(2)
C7–H72	1.03	N –O3(x, y, 1– $+z$)		2.823(2)
C7–H8	0.96			

This appears to be a general feature in amino acids even in the solid state where the energy of formation of hydrogen bonds is supposed to be greater than the energy barriers of rotation of the $C-NH_3$ bond (2–3 kcal). The preferred orientation of this group seems to be an important factor in the crystallization process in such a way that the requirements for a staggered conformation and the tetrahedral distribution of hydrogen bonds about the ammonium group can both be met with in the crystal.[11] This is an interesting point in the discussion of the degree of correspondence between the conformation of a molecule in the crystal as compared to that present in solution and in the gas phase. The $C-NH_3^+$ bond length (1.496 Å) is within the range normally reported for such bonds.[12–14] The C8–C9 bond length (1.534 Å) also closely agrees with the value found in other α-amino acids but is longer than the normal $C(sp^3)-C(sp^2)$ single bond.[15]

The geometry of the acid group is nearly identical to what was found in dihydroxyphenylalanine,[12] the carbon-oxygen bonds (1.246 Å and 1.260 Å) are not quite equal, the oxygen atom of the longer bond being involved in *two* hydrogen bonds whereas the other has only one such contact.

The nitrogen atom is situated 0.35 Å from the plane of the carboxyl group and the torsional angle N–C8–C9–O2 is 14°, which is close to the mean value for this angle.[15]

The conformation about the C7 – C8 bond is staggered, the C1 – C7 – C8 – C9 angle being 53.1° and the C1 – C7 – C8 – N 290.7°. Both the ammonium and the carboxyl groups are thus in *gauche* positions relative to the phenol moiety. The angle between the benzene ring plane and the one defined by the C1 – C7 – C8 atoms is 85.9°.

The C1 – C7 bond length is 1.516 Å as compared to 1.511 Å in L-tyrosine-*O*-sulfate dihydrate [14] and 1.512 Å in L-DOPA.[12]

The six atoms of the benzene ring are coplanar. Their deviations from a least-squares plane are given in Table 6.

Table 6. Deviations (Å) from a least-squares plane through the benzene ring atoms.

C1	0.007	C3	−0.001	C5	−0.007	O1	0.063
C2	−0.007	C4	0.008	C6	0.000	C7	0.060

The oxygen and carbon atoms bonded directly to the ring atoms are situated significantly out of this plane. The hydrogen atom HO1 is close to the benzene ring plane.

The C4 – O1 bond length is found to be 1.370 Å in accordance with what is usually observed in phenols and catechols but somewhat shorter than what might be expected from the covalent radii of C(sp^2) and O; a certain degree of delocalization of the electrons from the oxygen atom may account for this effect as well as for the tendency for the phenolic hydrogen atom to lie in the plane of the benzene ting. The external bond angles at the C4 atom are deformed relative to a symmetric arrangement in the same way as found in L-DOPA [12] and similar structures.

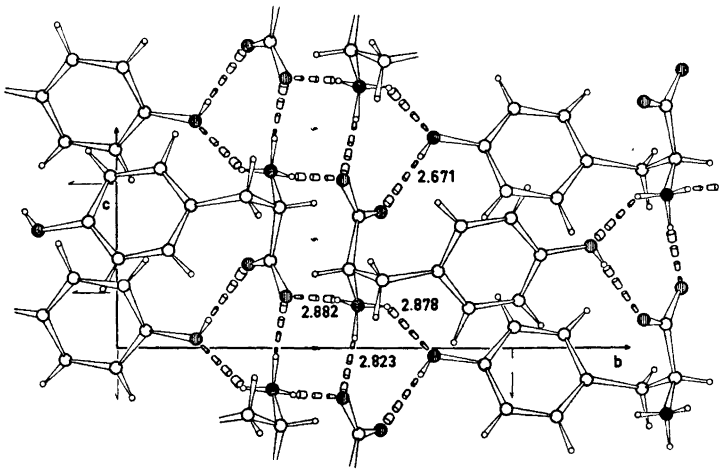

Fig. 2. The crystal structure as seen down the *a*-axis. The hydrogen bond lengths (Å) are indicated.

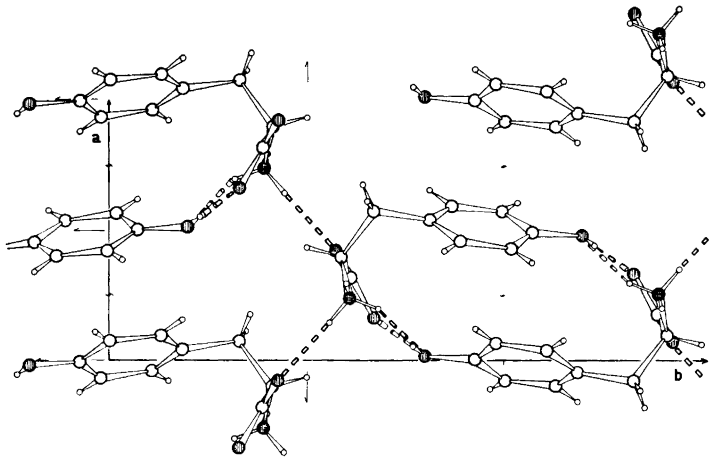

Fig. 3. The crystal structure as seen along the *c*-axis.

The mean carbon-carbon bond length in the benzene ring is 1.394 Å with a maximum deviation of 0.006 Å.

A crystal structure is characterized by a three-dimensional hydrogen bond network as visualized in Figs. 2 and 3. The nitrogen atom is hydrogen donor in three hydrogen bonds, two to carboxyl oxygen atoms of two different molecules (2.882 and 2.823 Å) and one to a phenolic oxygen atom of a third (2.878 Å). The phenolic hydrogen atom participate in a hydrogen bond to a carboxylic oxygen atom of a neighbouring molecule (2.671 Å). Each L-tyrosine molecule is hydrogen bonded to six neighbouring molecules.

Acknowledgement. The authors express their gratitude to cand. real. Per Groth for his advice in connection with the practical applications of direct methods.

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Received May 2, 1972.