ACTA CHEMICA SCANDINAVICA 27 (1973) 401–410

Crystal Structure of DL-Tyrosine

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The crystal structure of DL-tyrosine has been determined by X-ray methods using 1180 observed reflections collected by counter methods. The crystals are orthorhombic, space group $Pna2_1$, with unit cell dimensions $a = 20.83_6$ Å, $b = 6.81_0$ Å, and $c = 5.90_5$ Å. The structure was solved by direct methods and refined to a conventional R-factor of 0.037; estimated standard deviations in bond lengths not involving hydrogen are 0.003 Å and in angles 0.2°. The molecular dimensions are found to be nearly identical with those found for L-tyrosine. The difference in crystal packing between the L and the DL form is discussed.

The preferred conformation of tyrosine is of interest in several biochemical relations and has frequently been discussed. Information on the structure of the molecule in solution is difficult to obtain; one approach to the problem is to examine the molecular structure in various crystal modifications in order to study the influence of the environment on the conformation. For an optically active compound crystals of the active and racemic forms may both be examined.

The conformation of tyrosine in the crystals of L-tyrosine [1] is different from that in L-tyrosine hydrochloride [2] but is the same as the one reported for L-phenylalanine hydrochloride [3] and potassium L-tyrosine-*o*-sulphate dihydrate.[4] We have now investigated the crystal structure of DL-tyrosine in which the molecular packing necessarily is different from that in L-tyrosine. Furthermore, as the crystal data on L-tyrosine were found to be different from those derived from powder data,[5] we felt that the crystal data on DL-tyrosine arrived at from powder photographs [6] ought to be checked against single crystal results.

EXPERIMENTAL

DL-Tyrosine was recrystallized following the same procedure as the one worked out for L-tyrosine.[7] A single crystal with approximate dimensions $0.2 \times 0.25 \times 0.35$ mm^3 was mounted with the direction of the largest dimension (c) along the goniometer head axis and used in all the X-ray experiments.

Precession photographs indicate orthorhombic symmetry; space group extinctions are $(0kl)$ for $k+l$ odd and $(h0l)$ for h odd. The absence of centers of symmetry was proved by Wilson statistics; the space group is thus $Pna2_1$.

Unit cell dimensions were determined from diffractometer measurements on 30 general reflections using Mo$K(\alpha_1+\alpha_2)$ radiation ($\lambda=0.71069$ Å). It may be noted that one axis (6.810 Å) has half the length of that derived from powder data (13.68 Å).[6]

The intensity data were recorded with the use of a SYNTEX P$\bar{1}$ diffractometer with graphite crystal monochromated MoK radiation for 1369 independent reflections with $2\theta < 60°$ using the $\omega-2\theta$ scanning mode with scan speed varying from 2 to 12° min^{-1} dependent on the intensity. The scan range was from 1° below 2θ (α_1) to 1° above 2θ (α_2) and background counts were taken for half the scan time at each of the scan range limits. Three standard reflections measured after every 50 reflections showed no systematic fluctuation during the experiment. The 1180 reflections greater than $2.5\sigma(I)$ were considered to be observed; the remaining 189 were excluded from the structure refinement procedure.

The structure determination was based on the program MULTAN written by P. Main, M. M. Woolfson and G. Germain. All other computer programs applied are described in Ref. 10.

Atomic form factors used were those of Doyle and Turner [8] for oxygen, nitrogen, and carbon atoms and of Stewart, Davidson and Simpson [9] for hydrogen.

CRYSTAL DATA

DL-4-Hydroxyphenylalanine (DL-tyrosine) $C_9H_{11}O_3N$, orthorhombic. $a=20.836$ (0.0008) Å; $b=6.810$ (0.002) Å; $c=5.905$ (0.002) Å. $V=837.9$ Å^3, $M=181.19$, $F(000)=384$, $Z=4$, $D_{calc}=1.435$ g cm^{-3}. Absent reflections: $(0kl)$ for $k+l$ odd, $(h0l)$ for h odd. Space group $Pna2_1$.

STRUCTURE DETERMINATION

The intensity data were put on an absolute scale by Wilson's statistical method and normalized structure amplitudes were calculated. The 154 of these with E-values larger than 1.50 were used as input in the program assembly MULTAN.[11] Of the solutions obtained the one with the highest figure of merit was used as the basis for an E-map which readily indicated the positions of all non-hydrogen atoms. Initial least-squares refinement included the thirteen heavy atoms with isotropic, then anisotropic temperature factors. When the R-factor reached 0.05 all hydrogen atoms were assigned coordinates from stereochemical considerations and were included in the further least-squares calculations with individual isotropic thermal parameters. After five cycles the shifts in the parameters were negligible compared to the corresponding standard deviations. The final conventional R-factor was 0.037 and the weighted R was 0.055. 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 vibrations are given in Table 4. An analysis of the thermal parameters showed that the phenol and alanine parts may each be regarded as rigid bodies. The phenol part has the axis of the largest oscillation (4.6°) nearly parallel to the O1 – C4 – C1 – C7 direction; the alanine part has the corresponding axis (7.9°) parallel to the C8 – O3 direction. The bond lengths were corrected for librational effects according to this model.

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

2 0 0	55	55	11 4 0	33	29	24 0 1	23	20	18 4 1	53	52	18 0 2	61	62	12 4 2	102	101
4 0 0	353	353	12 4 0	110	111	26 0 1	79	76	19 4 1	29	29	20 0 2	29	21	13 4 2	201	202
6 0 0	292	286	13 4 0	183	190	28 0 1	82	74	20 4 1	36	36	22 0 2	20	26	14 4 2	144	146
8 0 0	555	558	14 4 0	141	135	0 1 1	1022	1008	21 4 1	47	43	24 0 2	71	70	15 4 2	42	44
10 0 0	616	603	16 4 0	43	43	1 1 1	144	131	22 4 1	52	52	26 0 2	87	87	16 4 2	114	113
12 0 0	18	16	17 4 0	68	67	2 1 1	415	417	23 4 1	65	62	28 0 2	83	80	17 4 2	126	129
13 0 0	22	8	18 4 0	88	90	3 1 1	249	241	24 4 1	32	26	1 1 2	190	179	18 4 2	36	32
14 0 0	38	36	19 4 0	36	38	4 1 1	243	233	25 4 1	40	40	2 1 2	386	375	19 4 2	35	35
16 0 0	74	67	20 4 0	121	118	5 1 1	243	233	0 5 1	37	39	3 1 2	399	394	20 4 2	29	33
18 0 0	159	178	21 4 0	48	50	6 1 1	257	248	1 5 1	182	181	4 1 2	478	455	21 4 2	53	53
20 0 0	185	196	22 4 0	41	42	7 1 1	196	188	2 5 1	93	98	5 1 2	325	321	22 4 2	66	64
22 0 0	57	53	23 4 0	42	43	8 1 1	126	123	3 5 1	93	90	6 1 2	96	84	23 4 2	31	28
24 0 0	49	87	24 4 0	48	50	9 1 1	72	73	4 5 1	48	43	7 1 2	150	161	25 4 2	41	42
26 0 0	73	73	25 4 0	22	24	10 1 1	297	286	5 5 1	20	19	8 1 2	188	182	1 5 2	78	77
28 0 0	25	18	26 4 0	35	37	11 1 1	73	72	6 5 1	114	110	9 1 2	202	202	2 5 2	89	88
1 1 0	203	202	2 5 0	190	184	12 1 1	156	161	7 5 1	142	138	10 1 2	96	87	3 5 2	45	43
2 1 0	327	338	3 5 0	96	89	13 1 1	174	170	8 5 1	27	30	11 1 2	150	149	4 5 2	229	228
3 1 0	648	666	5 5 0	29	31	14 1 1	204	201	9 5 1	114	110	12 1 2	73	71	5 5 2	204	200
4 1 0	268	277	6 5 0	99	108	15 1 1	29	34	10 5 1	62	64	13 1 2	107	106	6 5 2	118	124
5 1 0	698	722	7 5 0	126	129	16 1 1	96	96	11 5 1	48	50	14 1 2	160	170	7 5 2	85	84
6 1 0	443	435	8 5 0	39	42	17 1 1	65	69	12 5 1	66	69	15 1 2	132	137	8 5 2	25	25
7 1 0	363	380	9 5 0	90	95	18 1 1	51	57	13 5 1	95	96	16 1 2	155	154	9 5 2	44	43
8 1 0	399	383	10 5 0	37	31	19 1 1	78	78	14 5 1	143	145	18 1 2	191	195	10 5 2	73	71
9 1 0	111	114	11 5 0	125	125	20 1 1	121	123	15 5 1	120	122	19 1 2	40	39	11 5 2	27	31
10 1 0	205	188	12 5 0	48	46	21 1 1	42	46	16 5 1	66	68	20 1 2	50	52	12 5 2	60	61
12 1 0	351	355	13 5 0	79	79	23 1 1	26	28	17 5 1	75	74	21 1 2	27	31	14 5 2	37	37
13 1 0	206	207	14 5 0	34	33	24 1 1	22	25	18 5 1	69	74	22 1 2	85	83	15 5 2	126	124
14 1 0	151	145	15 5 0	99	101	25 1 1	43	39	19 5 1	34	35	23 1 2	37	36	17 5 2	47	44
15 1 0	107	104	16 5 0	46	42	26 1 1	74	71	20 5 1	44	41	24 1 2	77	76	18 5 2	91	89
16 1 0	144	136	17 5 0	40	42	28 1 1	73	64	21 5 1	28	29	25 1 2	29	38	19 5 2	29	38
17 1 0	112	112	18 5 0	80	81	1 2 1	443	425	22 5 1	54	57	26 1 2	63	59	21 5 2	27	25
18 1 0	50	51	19 5 0	31	28	2 2 1	223	216	24 5 1	38	35	27 1 2	54	54	22 5 2	52	46
19 1 0	54	52	20 5 0	74	74	3 2 1	382	372	1 6 1	25	19	28 1 2	55	56	23 5 2	24	22
20 1 0	124	133	21 5 0	24	12	4 2 1	216	214	2 6 1	109	109	0 2 2	446	431	0 6 2	170	176
22 1 0	27	28	22 5 0	81	85	5 2 1	36	30	3 6 1	148	149	1 2 2	198	190	1 6 2	117	121
23 1 0	31	28	23 5 0	53	52	6 2 1	193	184	4 6 1	187	184	2 2 2	303	300	2 6 2	195	200
25 1 0	40	40	0 6 0	131	136	7 2 1	211	200	6 6 1	38	38	3 2 2	121	120	3 6 2	75	76
26 1 0	32	35	2 6 0	33	34	8 2 1	98	101	7 6 1	70	69	4 2 2	223	207	4 6 2	70	73
27 1 0	51	54	3 6 0	49	45	9 2 1	207	206	8 6 1	46	48	5 2 2	195	188	5 6 2	45	42
28 1 0	74	71	4 6 0	134	135	10 2 1	237	223	9 6 1	46	45	6 2 2	103	97	6 6 2	75	76
1 2 0	75	72	5 6 0	25	22	11 2 1	140	132	10 6 1	84	79	7 2 2	126	122	7 6 2	36	40
2 2 0	721	732	6 6 0	47	43	12 2 1	139	134	11 6 1	47	46	8 2 2	145	142	8 6 2	69	72
3 2 0	544	543	7 6 0	104	102	13 2 1	171	170	12 6 1	70	70	9 2 2	72	73	9 6 2	76	81
4 2 0	58	47	10 6 0	88	90	14 2 1	40	40	13 6 1	46	53	10 2 2	195	196	10 6 2	77	76
5 2 0	320	308	11 6 0	96	96	15 2 1	47	88	14 6 1	40	38	11 2 2	31	28	12 6 2	53	51
6 2 0	329	319	12 6 0	25	25	16 2 1	156	159	15 6 1	39	37	12 2 2	90	96	13 6 2	29	32
7 2 0	144	135	13 6 0	97	100	17 2 1	145	148	16 6 1	41	37	13 2 2	141	148	14 6 2	31	31
8 2 0	231	223	14 6 0	203	200	18 2 1	64	68	17 6 1	67	70	14 2 2	195	199	15 6 2	28	32
9 2 0	72	68	15 6 0	77	81	20 2 1	30	34	18 6 1	67	66	15 2 2	42	44	16 6 2	40	41
10 2 0	44	41	16 6 0	50	51	21 2 1	32	31	19 6 1	35	35	16 2 2	161	167	17 6 2	57	61
11 2 0	323	313	17 6 0	45	44	23 2 1	42	43	20 6 1	36	34	17 2 2	44	45	19 6 2	26	26
12 2 0	47	47	18 6 0	66	65	24 2 1	37	37	22 6 1	27	24	18 2 2	123	122	20 6 2	45	41
13 2 0	414	408	19 6 0	49	47	25 2 1	24	23	0 7 1	58	61	19 2 2	103	106	1 7 2	79	80
15 2 0	67	70	22 6 0	47	42	26 2 1	29	33	1 7 1	86	89	20 2 2	72	71	2 7 2	22	22
16 2 0	142	143	1 7 0	74	76	28 2 1	42	43	2 7 1	49	48	22 2 2	24	31	3 7 2	52	54
18 2 0	145	132	2 7 0	145	150	0 3 1	354	342	3 7 1	49	48	23 2 2	37	36	4 7 2	75	74
19 2 0	131	135	3 7 0	47	49	1 3 1	327	323	4 7 1	29	24	24 2 2	43	42	7 7 2	99	100
20 2 0	52	60	4 7 0	36	35	2 3 1	249	242	5 7 1	28	25	25 2 2	39	37	8 7 2	27	25
21 2 0	43	36	5 7 0	26	22	3 3 1	330	320	6 7 1	63	61	26 2 2	44	47	9 7 2	39	38
22 2 0	70	72	6 7 0	77	78	4 3 1	156	152	7 7 1	61	59	27 2 2	81	82	10 7 2	53	53
23 2 0	41	46	9 7 0	112	111	5 3 1	165	158	8 7 1	45	44	1 3 2	130	123	11 7 2	32	33
26 2 0	73	72	10 7 0	36	33	6 3 1	162	162	9 7 1	88	85	2 3 2	260	253	12 7 2	56	55
28 2 0	77	77	14 7 0	24	14	7 3 1	127	133	10 7 1	31	29	3 3 2	200	193	13 7 2	25	25
1 3 0	64	61	16 7 0	79	75	8 3 1	87	81	11 7 1	97	93	4 3 2	94	98	15 7 2	37	35
2 3 0	17	23	17 7 0	79	80	9 3 1	79	81	12 7 1	92	90	5 3 2	260	247	17 7 2	44	40
3 3 0	48	54	18 7 0	57	56	10 3 1	46	49	13 7 1	29	32	6 3 2	108	95	18 7 2	58	58
4 3 0	127	111	0 8 0	63	68	11 3 1	177	176	14 7 1	46	48	7 3 2	161	161	0 8 2	79	79
5 3 0	89	79	1 8 0	48	47	12 3 1	108	109	15 7 1	36	38	8 3 2	192	188	1 8 2	35	38
6 3 0	47	39	3 8 0	30	26	13 3 1	122	129	16 7 1	51	52	9 3 2	201	203	2 8 2	71	72
7 3 0	130	128	4 8 0	36	33	14 3 1	199	198	17 7 1	73	68	10 3 2	17	19	3 8 2	45	49
8 3 0	135	127	5 8 0	28	26	15 3 1	103	104	18 7 1	31	35	11 3 2	98	97	4 8 2	65	66
9 3 0	142	146	6 8 0	42	49	16 3 1	128	132	19 7 1	60	60	12 3 2	58	58	5 8 2	91	90
10 3 0	204	196	7 8 0	51	47	17 3 1	44	46	1 8 1	24	25	13 3 2	115	119	6 8 2	26	26
11 3 0	214	220	8 8 0	37	38	18 3 1	64	68	2 8 1	49	48	14 3 2	33	37	7 8 2	33	33
12 3 0	150	145	9 8 0	26	23	19 3 1	32	27	3 8 1	55	55	15 3 2	234	237	9 8 2	49	50
13 3 0	37	37	10 8 0	46	47	20 3 1	86	86	4 8 1	68	64	16 3 2	143	144	10 8 2	24	23
14 3 0	55	67	11 8 0	77	77	22 3 1	59	61	5 8 1	40	36	17 3 2	93	91	11 8 2	45	48
15 3 0	41	41	12 8 0	76	74	23 3 1	27	33	6 8 1	62	61	18 3 2	73	74	12 8 2	32	29
16 3 0	76	72	13 8 0	55	54	24 3 1	36	40	8 8 1	50	50	19 3 2	60	60	13 8 2	62	59
17 3 0	39	41	14 8 0	65	62	25 3 1	57	50	9 8 1	67	68	20 3 2	35	31	1 9 2	49	49
18 3 0	84	79	15 8 0	40	37	27 3 1	34	32	10 8 1	44	43	21 3 2	32	30	2 9 2	23	30
19 3 0	51	52	16 8 0	28	32	1 4 1	187	186	12 8 1	51	50	22 3 2	75	76	3 9 2	33	32
20 3 0	39	39	1 9 0	51	56	2 4 1	296	295	14 8 1	31	27	23 3 2	41	41	4 9 2	45	41
21 3 0	60	57	2 9 0	34	33	3 4 1	298	295	15 8 1	33	32	25 3 2	67	61	6 9 2	24	22
22 3 0	36	38	3 9 0	24	5	4 4 1	67	64	0 9 1	48	49	26 3 2	39	37	7 9 2	34	37
23 3 0	65	65	4 9 0	30	28	5 4 1	103	100	1 9 1	38	37	27 3 2	54	49	2 0 3	419	404
24 3 0	86	82	9 9 0	82	81	6 4 1	176	168	3 9 1	32	32	0 4 2	129	129	4 0 3	133	127
25 3 0	88	86	2 0 1	219	216	7 4 1	62	53	7 9 1	43	43	1 4 2	142	141	6 0 3	197	187
1 4 0	48	49	4 0 1	453	449	8 4 1	64	58	8 9 1	33	29	2 4 2	154	153	8 0 3	220	210
2 4 0	182	179	6 0 1	200	178	9 4 1	45	46	0 0 2	435	429	3 4 2	177	173	10 0 3	218	220
3 4 0	246	246	8 0 1	75	77	10 4 1	89	88	2 0 2	401	391	4 4 2	86	79	12 0 3	232	233
4 4 0	76	73	10 0 1	366	353	11 4 1	51	52	4 0 2	411	403	5 4 2	150	158	14 0 3	239	245
5 4 0	46	50	12 0 1	90	91	12 4 1	59	57	6 0 2	476	459	6 4 2	21	25	16 0 3	145	142
6 4 0	163	167	14 0 1	94	94	13 4 1	65	69	8 0 2	247	252	7 4 2	26	30	18 0 3	99	84
7 4 0	65	63	16 0 1	106	106	14 4 1	55	57	10 0 2	55	59	8 4 2	112	109	20 0 3	63	65
8 4 0	45	45	18 0 1	134	139	15 4 1	227	232	12 0 2	149	148	9 4 2	113	110	22 0 3	47	50
9 4 0	22	25	20 0 1	76	88	16 4 1	45	48	14 0 2	215	216	10 4 2	40	41	24 0 3	125	123
10 4 0	78	70	22 0 1	54	51	17 4 1	69	66	16 0 2	329	344	11 4 2	128	132	26 0 3	24	32

Table 1. Continued.

0 1 3	229	232	5 5 3	44	42	10 2 4	82	79	14 7 4	31	26	1 5 5	57	53	3 4 6	27	29
1 1 3	133	133	7 5 3	127	127	11 2 4	176	189	0 9 4	76	74	2 5 5	22	26	4 4 6	23	11
2 1 3	341	324	9 5 3	43	44	12 2 4	54	55	1 9 4	29	31	3 5 5	39	37	5 4 6	51	51
3 1 3	34	36	9 5 3	82	91	13 2 4	72	71	2 8 4	31	23	4 5 5	39	37	6 4 6	65	67
4 1 3	109	102	10 5 3	57	66	14 2 4	86	89	3 8 4	25	20	5 5 5	22	25	7 4 6	54	54
5 1 3	156	152	12 5 3	89	90	15 2 4	45	44	8 8 4	32	26	6 5 5	36	37	8 4 6	40	44
6 1 3	170	162	14 5 3	50	51	16 2 4	22	20	2 0 5	290	302	7 5 5	47	50	9 4 6	27	22
7 1 3	125	123	15 5 3	46	44	17 2 4	76	82	4 0 5	171	172	8 5 5	71	74	10 4 6	33	37
8 1 3	82	80	16 5 3	52	49	18 2 4	27	31	6 0 5	221	224	9 5 5	33	34	12 4 6	34	31
9 1 3	95	93	17 5 3	31	35	19 2 4	78	82	8 0 5	217	237	10 5 5	62	61	13 4 6	59	60
10 1 3	68	67	18 5 3	66	62	21 2 4	73	74	10 0 5	82	81	11 5 5	30	30	14 4 6	37	39
11 1 3	33	32	19 5 3	75	76	22 2 4	44	45	12 0 5	30	26	12 5 5	59	55	15 4 6	54	52
12 1 3	178	181	22 5 3	30	30	24 2 4	42	41	14 0 5	137	150	13 5 5	64	65	16 4 6	46	45
13 1 3	81	80	1 6 3	113	113	1 3 4	210	215	16 0 5	60	59	14 5 5	73	73	1 5 6	52	54
14 1 3	153	155	2 6 3	76	76	2 3 4	100	103	18 0 5	111	113	16 5 5	34	36	3 5 6	27	21
15 1 3	95	99	3 6 3	35	33	3 3 4	144	148	20 0 5	85	80	17 5 5	29	25	4 5 6	94	90
16 1 3	259	263	4 6 3	61	57	4 3 4	78	83	22 0 5	66	68	1 6 5	48	51	5 5 6	121	120
18 1 3	67	70	5 6 3	51	48	5 3 4	78	75	0 1 5	213	215	2 6 5	46	48	6 5 6	56	55
19 1 3	96	94	6 6 3	84	83	6 3 4	118	124	1 1 5	213	215	4 6 5	40	43	7 5 6	31	29
20 1 3	23	29	7 6 3	57	61	7 3 4	82	83	2 1 5	182	183	5 6 5	37	36	8 5 6	29	34
24 1 3	82	79	8 6 3	54	49	8 3 4	23	20	3 1 5	111	118	6 6 5	87	86	9 5 6	57	52
26 1 3	50	45	9 6 3	43	43	9 3 4	144	142	4 1 5	201	202	8 6 5	54	53	10 5 6	24	27
27 1 3	50	47	10 6 3	79	83	10 3 4	81	88	5 1 5	68	65	9 6 5	78	78	11 5 6	33	32
1 2 3	218	217	12 6 3	71	68	11 3 4	84	85	6 1 5	34	40	10 6 5	53	58	12 5 6	52	46
2 2 3	173	169	13 6 3	25	26	12 3 4	97	96	7 1 5	125	125	11 6 5	46	48	0 6 6	102	102
3 2 3	151	144	14 6 3	50	48	13 3 4	127	133	8 1 5	117	121	12 6 5	39	34	1 6 6	59	52
4 2 3	327	311	15 6 3	29	25	14 3 4	138	144	9 1 5	125	129	14 6 5	56	51	2 6 6	46	45
5 2 3	132	127	18 6 3	59	61	16 3 4	108	99	10 1 5	57	61	0 7 5	87	87	3 6 6	40	40
6 2 3	121	124	19 6 3	63	61	17 3 4	114	117	11 1 5	107	113	1 7 5	26	29	4 6 6	27	26
7 2 3	157	157	20 6 3	38	35	18 3 4	57	59	12 1 5	89	89	3 7 5	57	52	5 6 6	26	28
8 2 3	177	180	0 7 3	134	136	19 3 4	65	64	13 1 5	63	63	4 7 5	43	39	6 6 6	26	30
9 2 3	62	65	1 7 3	74	74	20 3 4	28	31	14 1 5	159	169	6 7 5	36	39	8 6 6	65	67
11 2 3	101	99	2 7 3	120	120	21 3 4	55	52	15 1 5	52	46	8 7 5	36	35	2 0 7	123	114
12 2 3	180	185	3 7 3	67	69	22 3 4	33	33	16 1 5	65	66	9 7 5	33	27	4 0 7	144	142
13 2 3	105	112	4 7 3	54	53	23 3 4	25	24	18 1 5	47	44	0 0 6	80	79	6 0 7	161	160
14 2 3	89	86	5 7 3	72	74	24 3 4	66	60	19 1 5	51	52	2 0 6	93	83	8 0 7	96	89
15 2 3	122	126	6 7 3	91	87	0 4 4	252	264	20 1 5	78	73	4 0 6	147	151	10 0 7	55	55
16 2 3	136	139	7 7 3	31	32	1 4 4	82	78	21 1 5	47	47	6 0 6	102	103	12 0 7	36	34
17 2 3	88	89	8 7 3	30	29	2 4 4	78	80	22 1 5	38	37	8 0 6	35	42	14 0 7	50	47
18 2 3	89	91	9 7 3	45	44	3 4 4	67	70	23 1 5	47	45	10 0 6	31	32	0 1 7	124	117
19 2 3	77	77	12 7 3	75	73	4 4 4	33	32	1 2 5	72	70	12 0 6	59	57	1 1 7	116	116
20 2 3	35	37	13 7 3	42	40	5 4 4	41	44	2 2 5	145	142	14 0 6	121	123	2 1 7	51	49
21 2 3	96	95	14 7 3	54	55	6 4 4	55	61	3 2 5	104	109	16 0 6	63	63	3 1 7	47	47
22 2 3	39	41	16 7 3	42	42	7 4 4	80	78	4 2 5	153	156	18 0 6	38	41	6 1 7	32	32
23 2 3	82	79	1 8 3	66	68	8 4 4	112	113	5 2 5	131	136	20 0 6	39	36	7 1 7	79	75
25 2 3	27	28	2 8 3	33	34	9 4 4	79	85	6 2 5	95	98	2 1 6	121	121	8 1 7	32	29
26 2 3	64	63	4 8 3	47	44	10 4 4	49	49	7 2 5	95	99	3 1 6	62	61	9 1 7	83	81
0 3 3	98	101	5 8 3	27	29	11 4 4	100	105	8 2 5	93	97	4 1 6	117	120	10 1 7	106	101
1 3 3	209	206	6 8 3	25	28	12 4 4	56	55	9 2 5	50	52	5 1 6	56	56	11 1 7	41	38
2 3 3	70	69	7 8 3	46	47	13 4 4	58	63	11 2 5	89	90	8 1 6	110	118	13 1 7	51	50
3 3 3	154	156	9 8 3	27	20	15 4 4	57	56	12 2 5	101	104	9 1 6	49	48	14 1 7	52	51
4 3 3	43	45	10 8 3	44	45	18 4 4	33	30	13 2 5	50	53	10 1 6	51	52	1 2 7	63	62
5 3 3	98	98	12 8 3	43	39	19 4 4	60	62	14 2 5	43	47	12 1 6	31	31	2 2 7	39	39
6 3 3	164	163	0 0 4	150	162	20 4 4	41	39	15 2 5	38	36	13 1 6	21	12	4 2 7	73	64
7 3 3	98	95	2 0 4	137	145	22 4 4	36	46	16 2 5	55	57	14 1 6	41	41	5 2 7	95	91
8 3 3	17	11	4 0 4	55	48	1 5 4	207	211	17 2 5	69	70	15 1 6	64	60	7 2 7	108	107
9 3 3	109	108	6 0 4	154	154	2 5 4	31	33	18 2 5	66	66	16 1 6	76	69	8 2 7	65	64
10 3 3	80	81	8 0 4	126	135	3 5 4	51	55	19 2 5	35	41	17 1 6	28	29	9 2 7	43	46
11 3 3	133	147	10 0 4	18	22	5 5 4	95	98	20 2 5	43	43	18 1 6	60	57	10 2 7	36	34
12 3 3	160	163	12 0 4	145	150	7 5 4	24	22	21 2 5	41	41	19 1 6	32	30	11 2 7	54	51
13 3 3	122	127	14 0 4	133	129	8 5 4	59	65	0 3 5	109	109	0 2 6	24	27	12 2 7	69	72
14 3 3	63	57	16 0 4	27	28	9 5 4	64	65	1 3 5	59	60	1 2 6	56	57	13 2 7	57	54
15 3 3	110	118	18 0 4	51	54	10 5 4	57	60	2 3 5	79	84	2 2 6	58	60	14 2 7	24	25
16 3 3	59	59	20 0 4	85	81	11 5 4	124	121	3 3 5	110	108	3 2 6	52	55	0 3 7	72	71
17 3 3	107	112	22 0 4	41	40	12 5 4	102	101	4 3 5	41	35	4 2 6	99	97	1 3 7	54	54
18 3 3	88	88	24 0 4	83	81	13 5 4	23	22	5 3 5	40	47	5 2 6	76	76	3 3 7	31	35
19 3 3	64	66	1 1 4	117	117	15 5 4	29	25	6 3 5	55	57	6 2 6	48	45	4 3 7	41	43
20 3 3	89	88	2 1 4	229	230	16 5 4	25	24	9 3 5	22	26	7 2 6	45	49	5 3 7	72	71
21 3 3	99	87	3 1 4	128	133	17 5 4	24	25	10 3 5	77	80	8 2 6	32	34	9 3 7	35	36
22 3 3	26	29	4 1 4	133	107	18 5 4	65	61	11 3 5	130	135	9 2 6	32	37	10 3 7	43	36
23 3 3	45	44	5 1 4	78	70	19 5 4	78	76	12 3 5	31	33	10 2 6	41	42	11 3 7	35	38
24 3 3	24	33	6 1 4	90	91	20 5 4	89	92	13 3 5	62	60	11 2 6	49	50	12 3 7	65	60
25 3 3	28	29	7 1 4	32	32	0 6 4	117	118	14 3 5	51	51	12 2 6	48	50	13 3 7	91	88
1 4 3	159	164	8 1 4	115	122	1 6 4	25	17	15 3 5	54	54	13 2 6	36	38	1 4 7	62	64
2 4 3	43	42	9 1 4	109	105	2 6 4	76	77	17 3 5	113	111	14 2 6	43	45	2 4 7	35	32
3 4 3	65	69	10 1 4	34	33	3 6 4	26	25	18 3 5	53	53	15 2 6	29	34	4 4 7	67	68
4 4 3	169	177	11 1 4	45	49	5 6 4	35	34	19 3 5	49	45	16 2 6	34	32	5 4 7	120	116
5 4 3	106	109	12 1 4	153	155	6 6 4	49	47	20 3 5	29	32	17 2 6	71	72	6 4 7	53	49
6 4 3	151	158	13 1 4	66	63	7 6 4	47	45	21 3 5	40	38	19 2 6	36	36	7 4 7	54	53
7 4 3	128	129	14 1 4	96	99	8 6 4	54	52	1 4 5	96	95	1 3 6	24	20	8 4 7	28	27
8 4 3	81	78	15 1 4	41	46	10 6 4	58	59	2 4 5	48	45	2 3 6	61	60	0 5 7	55	54
9 4 3	91	92	16 1 4	57	57	11 6 4	36	41	3 4 5	56	51	3 3 6	104	108	2 5 7	41	39
10 4 3	127	129	17 1 4	34	33	12 6 4	28	29	4 4 5	55	57	4 3 6	81	83	3 5 7	34	29
11 4 3	60	63	18 1 4	73	73	13 6 4	34	36	5 4 5	94	88	5 3 6	75	75	4 5 7	46	46
12 4 3	46	50	19 1 4	35	31	15 6 4	38	38	6 4 5	41	45	6 3 6	63	66	0 0 8	129	124
13 4 3	21	16	20 1 4	33	31	16 6 4	35	34	7 4 5	62	63	7 3 6	94	91	2 0 8	92	89
14 4 3	85	89	21 1 4	27	32	17 6 4	46	46	8 4 5	47	51	8 3 6	70	68	6 0 8	51	46
15 4 3	89	91	22 1 4	100	99	18 6 4	65	63	9 4 5	74	78	9 3 6	23	16	8 0 8	50	49
16 4 3	37	39	23 1 4	30	26	1 7 4	36	35	11 4 5	116	112	10 3 6	24	21	1 1 8	27	24
17 4 3	35	33	24 1 4	26	27	2 7 4	44	42	12 4 5	82	82	12 3 6	41	43	3 1 8	45	49
18 4 3	97	99	0 2 4	73	72	3 7 4	51	49	13 4 5	43	42	13 3 6	33	37	4 1 8	37	36
19 4 3	88	83	1 2 4	63	64	4 7 4	67	63	14 4 5	35	35	14 3 6	49	48	5 1 9	44	43
20 4 3	43	44	2 2 4	192	205	5 7 4	69	64	15 4 5	80	76	15 3 6	73	74	0 2 8	28	26
21 4 3	60	59	3 2 4	132	139	6 7 4	25	20	16 4 5	64	63	17 3 6	51	59	1 2 8	58	55
0 5 3	97	98	5 2 4	55	56	7 7 4	26	25	17 4 5	37	39	18 3 6	63	57	2 2 8	91	90
1 5 3	159	165	6 2 4	74	69	8 7 4	46	49	18 4 5	37	32	0 4 6	52	50	3 2 8	38	38
2 5 3	200	204	7 2 4	62	60	9 7 4	51	53	19 4 5	32	32	1 4 6	27	25	4 2 8	25	24
3 5 3	79	75	8 2 4	45	45	10 7 4	46	48	20 4 5	59	58	2 4 6	40	48	5 2 8	25	21
4 5 3	34	34	9 2 4	26	18	12 7 4	37	38	0 5 5	132	135						

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	−10168	73060	17400	112	2000	1565	−117	−20	273
	7	27		3	39	49	17	22	81
O2	17158	40200	2030	169	1400	1506	−219	−126	−464
	8	24	44	4	31	44	17	22	68
O3	21463	67438	−12859	161	1659	1047	−103	51	30
	8	25	45	4	34	43	18	21	68
N	19866	49323	44313	113	1336	949	36	5	116
	8	26	45	3	35	40	17	21	71
C1	9488	79124	28302	108	933	1319	45	35	−78
	9	27	47	4	34	52	18	26	76
C2	6665	84401	7769	117	1136	1185	39	161	313
	9	30	50	4	37	49	20	26	77
C3	96	82104	4253	122	1182	1284	68	−48	202
	10	31	52	4	36	57	20	28	83
C4	−3696	74333	21334	104	972	1340	−15	31	−252
	9	29	48	4	35	55	19	26	79
C5	−970	68510	41867	122	1119	1247	−13	116	314
	10	31	52	4	35	53	20	26	78
C6	5619	71018	45145	123	1189	1151	117	53	284
	10	30	48	4	37	50	20	27	76
C7	16567	82769	32339	108	1115	1426	−30	18	−331
	9	29	48	4	35	61	19	24	76
C8	20904	65017	27242	87	1181	850	−76	−9	−81
	9	31	47	4	37	45	18	22	74
C9	19741	56741	3502	78	1294	931	54	−58	−460
	8	30	47	3	39	46	18	21	77

Standard deviations in bond lengths and angles were computed from the correlation matrix ignoring standard deviations in cell parameters. For distances and angles the standard deviations were calculated to be 0.003 Å and 0.2°, respectively, except for the bond lengths involving hydrogen where the standard deviation varied from 0.03 to 0.06 Å.

DISCUSSION

A drawing of the molecule is shown in Fig. 1 in which the numbering of the atoms is also indicated. The bond lengths (corrected for thermal effects) and valence angles are given in this figure; interactomic distances and bond angles are also listed in Table 5.

The unit cell dimensions for DL-tyrosine are quite close to those found for L-tyrosine,[1] and it is interesting to note that the same relation exists between the space groups of L- and DL-tyrosine as that reported for L- and DL-alanine,[12] *viz.* $P2_12_12_1$ for the optically active crystals and $Pna2_1$ for the racemate. It has recently been pointed out by Pedone and Benedetti[13] that such relations

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

Atom	x	y	z	B
H2	984	8954	−479	5.3
	23	69	112	1.2
H3	−202	8587	−1020	2.5
	13	41	75	0.6
H5	−367	6261	5327	2.1
	15	40	72	0.6
H6	721	6847	5787	4.5
	15	53	87	0.8
H71	1744	8652	4920	2.4
	17	49	91	0.9
H72	1773	9259	2367	1.6
	12	41	65	0.6
H8	2511	6857	3006	1.4
	15	41	60	0.6
HO1	−1170	6871	2893	5.1
	18	45	85	0.8
HN1	1668	4558	4428	5.8
	22	65	112	1.2
HN2	2018	5535	5782	4.8
	14	45	65	0.6
HN3	2284	3906	4282	3.4
	13	43	71	0.7

Table 4. R.m.s. amplitudes of vibration $(\overline{u^2})^{\frac{1}{2}}$ 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	$(\overline{u^2})^{\frac{1}{2}}$	B	e_x	e_y	e_z
	.219	3.80	−9	143	23
O1	.165	2.15	1	21	−168
	.155	1.89	47	26	6
	.208	3.41	−38	89	3
O2	.181	2.60	20	85	−118
	.143	1.63	21	81	121
	.203	3.26	26	−124	4
O3	.182	2.63	40	79	17
	.135	1.45	5	5	−168
	.178	2.51	9	144	13
N	.157	1.95	−47	28	1
	.129	1.32	0	12	−169
	.158	1.97	41	52	66
C1	.154	1.86	8	79	−140
	.143	1.61	−24	112	68
	.176	2.45	31	86	85
C2	.158	1.98	29	−115	23
	.132	1.37	23	32	−145

Table 4. Continued.

	.173	2.36	29	117	18
C3	.163	2.09	−34	68	91
	.145	1.66	18	−58	142
	.162	2.07	14	−89	124
C4	.150	1.77	45	41	−26
	.144	1.63	−5	109	112
	.171	2.32	33	69	93
C5	.164	2.13	−29	117	13
	.137	1.49	19	56	−141
	.181	2.58	31	107	44
C6	.153	1.85	−37	90	28
	.139	1.53	2	44	−161
	.171	2.32	10	−110	107
C7	.153	1.85	46	1	−52
	.149	1.75	11	98	121
	.169	2.25	13	−141	9
C8	.135	1.45	46	39	−24
	.122	1.18	6	13	167
	.179	2.54	8	138	−51
C9	.132	1.38	−43	39	63
	.120	1.14	21	30	149

may indeed be expected between crystals of the optically active and racemic compounds where virtually identical layers of molecules are packed through the operation of different symmetry elements. This appears to be the case in L- and DL-tyrosine, the layer of molecules between the diagonal glide-planes shown in Fig. 3 is nearly the same in both structures. The layers are differently

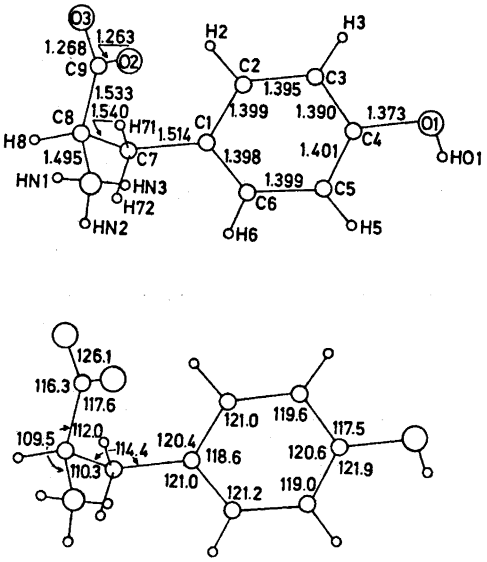

Fig. 1. Bond lengths (Å) corrected for thermal vibration effects and angles (°) in DL-tyrosine.

Table 5. Bond lengths (Å) and bond angles (°) in DL-tyrosine.

	Bond length	Corrected	Bond angle	
C1 – C2	1.395	1.399	C1 – C2 – C3	121.0
C2 – C3	1.393	1.395	C2 – C3 – C4	119.6
C3 – C4	1.386	1.390	C3 – C4 – C5	120.6
C4 – C5	1.396	1.401	C4 – C5 – C6	119.0
C5 – C6	1.397	1.399	C1 – C6 – C5	121.2
C1 – C6	1.394	1.398	C2 – C1 – C6	118.6
C1 – C7	1.513	1.514	C7 – C1 – C2	120.4
C7 – C8	1.540		C7 – C1 – C6	121.0
C8 – C9	1.530	1.533	O1 – C4 – C5	121.9
C8 – N	1.485	1.495	O1 – C4 – C3	117.5
C9 – O2	1.251	1.263	C1 – C7 – C8	114.4
C9 – O3	1.262	1.268	C7 – C8 – C9	112.0
C4 – O1	1.371	1.373	C7 – C8 – N	110.3
O1 – HO1	0.81		N – C8 – C9	109.5
N – H1N	0.70		C8 – C9 – O2	117.6
N – H2N	0.90		C8 – C9 – O3	116.3
N – H3N	0.94		O2 – C9 – O3	126.1
C2 – H2	1.05			
C3 – H3	0.99	Hydrogen bond lengths		
C5 – H5	0.97			
C6 – H6	0.84	O1 – O2($-x$, $1-y$, $\frac{1}{2}+z$)		2.668
C7 – H71	1.04	N – O1 ($-x$, $1-y$, $\frac{1}{2}+z$)		2.875
C7 – H72	0.87	N – O3 (x, y, $1+z$)		2.833
C8 – H8	0.92	N – O3 ($\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}+z$)		2.856

packed, however, as may be expected since all layers in L-tyrosine are identical whereas the layers in DL-tyrosine consist alternatingly of D and L forms. The difference in packing is visualized in Figs. 2 (A) and (B) which show the coupling of molecules of different layers through the alanine parts; (A) shows the conditions in L-tyrosine as viewed along the *a*-axis (6.913 Å) and (B) represents the DL-tyrosine structure as viewed down the *b*-axis (6.810 Å). The pertinent symmetry elements responsible for the coupling of layers are screw axes and glide-planes, respectively. The molecular packing is somewhat denser in the racemate, the density being 1.435 g cm^{-3} as compared to 1.414 g cm^{-3} for L-tyrosine.

The bond lengths and angles found in the present investigation are nearly identical to those determined from the study of the L-form. Except for the C9 – O2 bond in the carboxyl group the differences in corresponding bonds are insignificant, 0.008 Å or less; the C9 – O2 bond is found 0.017 Å longer than in L-tyrosine. The differences in corresponding angles are 0.7° or less, the largest dissimilarities are found in the alanine moiety. The conformation in the two structures are also equal; the angle between the phenyl ring plane and the plane defined by the C1 – C7 – C8 atoms is 85.8° (as compared to 85.9° in L-tyrosine), the dihedral angles C1 – C7 – C8 – C9 and C1 – C7 – C8 – N are 52.5° and 290.3, respectively (53.1° and 290.7° in L-tyrosine) whereas the torsional angle N – C8 – C9 – O2 is 11.7°, 2.3° less than the corresponding angle in L-tyrosine.

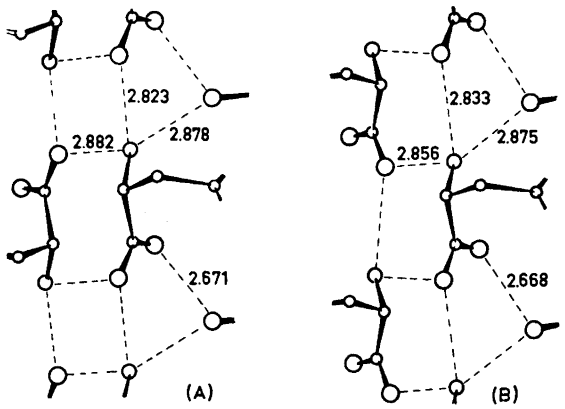

Fig. 2. Molecular arrangement in L-tyrosine (A) and in DL-tyrosine (B) crystals.

The hydrogen bond system in the crystals of DL-tyrosin is shown in Fig. 3. Each molecule is hydrogen donor as well as acceptor in four hydrogen bonds in such a way that one molecule is hydrogen bonded to six neighbouring molecules. The hydrogen bond lengths (given in Table 5) within the layers of molecules of equal chirality are nearly the same as the corresponding bonds in L-tyrosine; the hydrogen bonds linking the layers together are by 0.026 Å shorter in the racemate than in the crystals of the L-form.

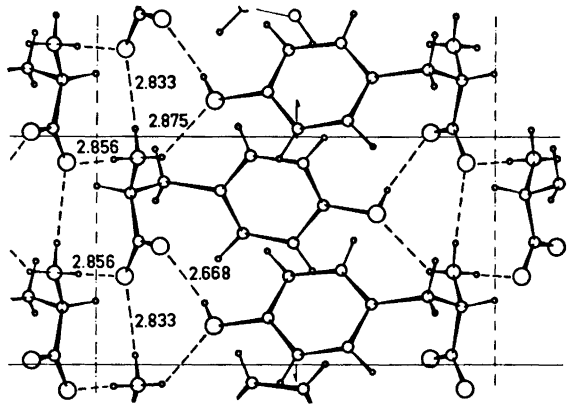

Fig. 3. The crystal structure of DL-tyrosine as viewed along the *b*-axis.

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Received August 11, 1972.