

hedra which share corner atoms with neighbouring tetrahedra. The tetrahedra formed by cations surrounding the anions are shown in projection along the [010] direction in Fig. 1. Three of these tetrahedra, corresponding to crystallographically different central sulphur atoms, are drawn in this Figure. The sulphur atom links to their nearest cations are shown by solid lines and edges of the tetrahedra are marked by broken lines.

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**On the unit-cell dimensions and space group of L-tyrosine and L-tryptophane.** By B. KHAWAS and G. S. R. KRISHNA MURTI, *Division of Agricultural Physics, Indian Agricultural Research Institute, New Delhi-12, India*

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The Debye-Scherrer patterns of L-tyrosine,  $\alpha$ -amino- $\beta$ -(*p*-hydroxyphenyl)propionic acid, and L-tryptophane,  $\alpha$ -amino-3-indolepropionic acid, have been analysed. L-Tyrosine, crystallized from aqueous solution, is orthorhombic, space group *Pnam*, with eight molecules per unit cell of dimensions  $a=13.89$ ,  $b=21.08$  and  $c=5.84_2$  Å. L-Tryptophane, crystallized from aqueous solution, is also orthorhombic, space group *Pmmm*, with eight molecules per unit cell of dimensions  $a=16.81$ ,  $b=17.90$  and  $c=6.90_4$  Å.

For the interpretation of X-ray diffraction photographs of animal materials like silk, keratin, proteins, etc. it is necessary to have a knowledge of the crystal structure of pure aminoacids. Bernal (1931) reported on the unit-cell dimensions of fifteen aminoacids; recently the dimorphism of DL-aspartic acid (Krishna Murti, Natarajan & Deb, 1965) and the unit-cell dimensions and the space group of DL-tryptophane and DL- $\beta$ -phenylalanine (Khawas & Krishna Murti, 1968) have been determined. The data on the crystal structure of L-tyrosine and L-tryptophane has not been reported so far.

The compounds could not be obtained as good single crystals by the ordinary methods of crystallization so information regarding the structure of these compounds had to be obtained from powder patterns alone; these were taken on a Philips 11.48 cm camera with Cu  $K\alpha$  radiation.

The spacings of the reflexions were calculated from measurements of the distances between arcs of symmetrical pairs in the powder patterns to an accuracy of 0.1 mm. The patterns could not be indexed in terms of a unit cell of cubic, tetragonal or hexagonal symmetry. The patterns were then analysed by a modification (Krishna Murti *et al.*, 1965) of Lipson's (1949) method.

#### L-Tyrosine

Pure L-tyrosine, obtained from the British Drug Houses Ltd., England, was crystallized from its aqueous solution, by evaporation at room temperature, in clusters of very fine needle-shaped crystals. The fibre pattern, about the fibre axis (Fig. 1), of such a bundle of crystals was also taken.

The values of the constants *A*, *B* and *C* from the analysis are found to be 0.00518, 0.00225 and 0.0293 respectively, where  $A=1/a^2$ ,  $B=1/b^2$  and  $C=1/c^2$ . There is good agreement between the observed and calculated  $Q(1/d_{hkl}^2)$  values as shown in Table 1.

Table 1. *Data on the powder pattern of L-tyrosine*

Intensity*	Spacing observed	$Q(1/d_{hkl}^2)$		Indices
		Observed	Calculated	
<i>m</i>	6.583 Å	0.0231	0.0229	210
<i>vw</i>	6.237	0.0257	0.0254	130

#### References

- BRAGG, W. L. & CLARINGBULL, G. F. (1965). *Crystal Structures of Minerals*, p. 45. London: Bell.  
 FRONDEL, C. (1941). *Amer. Min.* **26**, 25.  
 HARKER, D. (1936). *J. Chem. Phys.* **4**, 381.  
 WERNER, S. & FRAATZ (1910). *Cbl. Miner.* **331**.  
 WYCKOFF, R. W. G. (1921). *Amer. J. Sci.* **2**, 239.

Table 1 (cont.)

Intensity*	Spacing observed	$Q(1/d_{hkl}^2)$		Indices
		Observed	Calculated	
<i>s</i> (broad)	5.829 Å	0.0294	0.0297	220
<i>w</i>	5.624	0.0316	0.0315	011
<i>w</i>	5.294	0.0357	0.0360	040
			0.0367	111
<i>vs</i>	4.955	0.0407	0.0409	230
			0.0412	140
<i>m</i>	4.493	0.0495	0.0495	031
			0.0500	201
<i>vs</i>	4.376	0.0522	0.0522	211
<i>vw</i>	4.231	0.0559	0.0556	320
			0.0567	240
<i>m</i> (broad)	4.124	0.0588	0.0590	221
<i>s</i>	3.619	0.0764	0.0769	250
<i>s</i>	3.485	0.0823	0.0826	340
			0.0829	400
<i>s</i>	3.421	0.0854	0.0849	321
			0.0855	051
			0.0860	241
<i>s</i>	3.296	0.0921	0.0919	420
<i>s</i> (broad)	3.132	0.1019	0.1017	260
			0.1028	350
<i>m</i>	2.974	0.1131	0.1122	401
<i>w</i>	2.880	0.1206	0.1212	421
<i>vw</i>	2.822	0.1256	0.1262	022
<i>m</i>	2.754	0.1318	0.1310	261
			0.1314	351
			0.1321	122
<i>m</i>	2.679	0.1393	0.1385	520
			0.1391	450
			0.1401	212
<i>m</i>	2.614	0.1463	0.1469	222
<i>vw</i>	2.561	0.1525	0.1532	042
<i>vw</i>	2.519	0.1576	0.1569	361
			0.1581	232
			0.1584	142
<i>w</i>	2.475	0.1632	0.1639	460
<i>w</i>	2.404	0.1730	0.1728	322
			0.1732	242
<i>vwv</i>	2.336	0.1833	0.1841	332
<i>m</i>	2.279	0.1925	0.1932	461
<i>vw</i>	2.232	0.2007	0.2001	402
<i>vw</i>	2.183	0.2098	0.2091	422
			0.2105	560
<i>s</i>	2.149	0.2165	0.2158	601
			0.2167	191



Fig. 1. L-Tyrosine. Fibre pattern about the [001] axis, Cu  $K\alpha$  radiation; camera radius = 3 cm.

Table 1 (cont.)

Intensity* observed	Spacing	$Q$ ( $1/d_{hkl}^2$ )		Indices
		Observed	Calculated	
<i>m</i>	2.112 Å	0.2242	0.2248 0.2250	0,10,0 621
<i>vw</i>	2.085	0.2300	0.2302	1,10,0
<i>vw</i>	2.062	0.2352	0.2360	631
<i>vw</i>	2.027	0.2434	0.2427	650
<i>w</i>	1.993	0.2518	0.2518	641
<i>vw</i>	1.949	0.2633	0.2628	720
<i>w</i>	1.918	0.2718	0.2711 0.2716 0.2720	113 3,10,0 651
<i>w</i>	1.888	0.2805	0.2811	462
<i>w</i>	1.842	0.2947	0.2944	491
<i>vw</i>	1.818	0.3026	0.3028 0.3033	581 731
<i>vw</i>	1.791	0.3118	0.3125	313
<i>vw</i>	1.766	0.3206	0.3199 0.3201 0.3204	053 292 243
<i>w</i>	1.726	0.3357	0.3348	760
<i>w</i>	1.687	0.3514	0.3517	830
<i>w</i>	1.656	0.3647	0.3640 0.3641 0.3654	770 761 263
<i>m</i>	1.621	0.3806	0.3810	831
<i>vw</i>	1.590	0.3956	0.3954	513
<i>vw</i>	1.561	0.4104	0.4101	2,11,2
<i>vw</i> (broad)	1.526	0.4294	0.4286 0.4289 0.4292 0.4302	920 592 543 2,13,1
<i>vw</i>	1.487	0.4522	0.4520 0.4524	762 613
<i>vw</i>	1.479	0.4572	0.4568 0.4577 0.4579	473 822 921
<i>vw</i>	1.461	0.4685	0.4688 0.4689	004 832
<i>w</i>	1.433	0.4870	0.4862 0.4876 0.4878	643 3,14,0 3,12,2
<i>vw</i>	1.405	0.5066	0.5064	653
<i>w</i>	1.378	0.5266	0.5260 0.5265 0.5269 0.5270	7,11,0 723 2,15,0 10,2,0
<i>vw</i>	1.348	0.5503	0.5495 0.5498	10,1,1 064
<i>vw</i>	1.323	0.5713	0.5707 0.5716 0.5719	5,12,2 4,10,3; 354 434
<i>vw</i>	1.302	0.5899	0.5891	4,15,0
<i>vw</i>	1.287	0.6037	0.6035 0.6037 0.6042	10,5,3 8,11,0 823
<i>vw</i>	1.278	0.6123	0.6128	084
<i>vw</i>	1.263	0.6269	0.6269 0.6275 0.6277	5,13,2 6,14,0 6,12,2; 773
<i>vw</i>	1.252	0.6380	0.6374	10,1,2

\* *vs*, very strong; *s*, strong; *m*, medium; *w*, weak; *vw*, very weak; *vw*, very very weak.

The unit-cell dimensions are:  $a=13.89$  Å,  $b=21.08$ ,  $c=5.84_2$ . The repeat distance along the rotation axis of the fibre was calculated to be  $5.835$  Å. The fibre axis was thus identified as the [001] axis of the crystals. With the above cell dimensions the moderately strong spots in the fibre pattern could be indexed satisfactorily (Table 2). The

density of the compound is  $1.45$  g.cm<sup>-3</sup>. The number of molecules per unit cell was calculated to be  $8.24$ . Assuming  $Z=8$ , the calculated density is  $1.41$  g.cm<sup>-3</sup>.

Table 2. Data on the fibre pattern of L-tyrosine

Intensity	Spacing		Indices
	Observed	Calculated	
Zero layer line			
<i>m</i>	6.62 Å	6.61 Å	210
<i>s</i>	5.83	5.80	220
<i>w</i>	5.29	5.27	040
<i>vs</i>	4.94	4.94	230
		4.93	140
<i>m</i>	4.22	4.24	320
		4.20	240
<i>vs</i>	3.63	3.61	250
<i>vs</i>	3.49	3.48	340
		3.47	400
<i>vs</i>	3.30	3.30	420
<i>vs</i>	3.13	3.13	260
		3.12	350
<i>w</i>	2.80	2.80	360
<i>w</i> (broad)	2.68	2.69	520
		2.68	450
<i>m</i>	2.48	2.47	460
<i>m</i>	2.12	2.12	640
First layer line			
<i>s</i>	5.62	5.63	011
<i>vw</i>	5.18	5.22	111
<i>vs</i>	4.49	4.49	031
		4.47	201
<i>m</i>	4.14	4.12	221
<i>m</i>	3.44	3.43	321
		3.42	051
<i>vw</i>	3.07	3.07	251
<i>w</i>	2.98	2.99	341
		2.98	401
<i>w</i>	2.88	2.87	421
<i>m</i>	2.75	2.76	261
		2.75	351
<i>vw</i>	2.68	2.68	071
<i>vw</i>	2.62	2.63	171
<i>vw</i>	2.52	2.52	361
<i>w</i>	2.28	2.28	461
<i>m</i>	2.16	2.16	551
		2.15	601
Second layer line			
<i>m</i>	2.66	2.67	212
<i>m</i>	2.60	2.61	222
<i>w</i>	2.51	2.51	142
<i>w</i>	2.39	2.40	242
<i>w</i>	2.25	2.25	062
		2.24	402
<i>m</i>	2.13	2.13	432

\* *vs*, very strong; *s*, strong; *m*, medium; *w*, weak; *vw*, very weak.

The conditions limiting possible reflexions, as can be seen from Tables 1 and 2, are:  $hkl$ , no condition;  $hk0$ , no condition;  $0kl$ , ( $k+l$ ) odd;  $h0l$ ,  $h$  odd. The space group  $Pnam$  can thus be assigned to the crystal.

#### L-Tryptophane

Pure L-tryptophane, obtained from the British Drug Houses Ltd., U.S.A. was crystallized from its aqueous solution by evaporation at room temperature. The data (Table 3) were analysed and the constants  $A$ ,  $B$  and  $C$  are found to

Table 3. Data on the powder pattern of L-tryptophane

Number of lines (1)	Intensity* (2)	Spacing observed (3)	Observed $Q(1/d_{hkl}^2)$ (4)	Calculated (5)	Indices (6)
1	<i>vs</i>	17.330 Å	0.0033	0.0031 0.0035	010 100
2	<i>s</i>	8.976	0.0124	0.0125	020
3	<i>s</i>	6.008	0.0277	0.0276 0.0281	111 030
4	<i>w</i>	5.680	0.0310	0.0316 0.0319	130 300
5	<i>vw</i>	5.340	0.0351	0.0350 0.0351	310 201
6	<i>vs</i>	5.039	0.0394	0.0383	211
7	<i>vs</i>	4.821	0.0430	0.0422	230
8	<i>s</i>	4.484	0.0497	0.0491 0.0499	031 040
9	<i>vw</i>	4.241	0.0556	0.0560 0.0566	311 400
10	<i>vw</i>	4.086	0.0599	0.0598 0.0599	410 330
11	<i>w</i>	3.945	0.0643	0.0641 0.0653	240 321
12	<i>m</i>	3.825	0.0683	0.0691	420
13	<i>w</i>	3.678	0.0739	0.0744	141
14	<i>m</i>	3.576	0.0782	0.0776 0.0780	401 050
15	<i>vw</i>	3.427	0.0851	0.0847 0.0851	430 241
16	<i>vw</i>	3.301	0.0918	0.0916 0.0921	510 250
17	<i>vw</i>	3.089	0.1048	0.1057	431
18	<i>vw</i>	2.979	0.1127	0.1120 0.1123 0.1126 0.1131	032 060 511 251
19	<i>m</i>	2.871	0.1213	0.1220	521
20	<i>w</i>	2.774	0.1300	0.1306 0.1308	610 351
21	<i>vw</i> (broad)	2.679	0.1393	0.1384 0.1399	540 620
22	<i>w</i>	2.557	0.1529	0.1529 0.1530	070 422
23	<i>m</i> (broad)	2.488	0.1615	0.1609 0.1619	721 052
24	<i>w</i>	2.406	0.1727	0.1724 0.1735	502 700
25	<i>m</i>	2.297	0.1895	0.1888 0.1899	003 461
26	<i>vw</i>	2.241	0.1991	0.1983 0.1997 0.1998	641 080 162
27	<i>w</i>	2.178	0.2108	0.2104 0.2114	262 602
28	<i>vw</i>	2.103	0.2261	0.2264 0.2266	651 800
29	<i>vw</i>	2.045	0.2391	0.2387 0.2390 0.2394 0.2398	043 820 632 660
30	<i>w</i>	1.987	0.2533	0.2525 0.2527 0.2529	381 090 462; 243
31	<i>vw</i>	1.933	0.2676	0.2668 0.2669	053 290
32	<i>w</i>	1.879	0.2832	0.2836	082
33	<i>vw</i>	1.793	0.3111	0.3105 0.3108	802 911
34	<i>vw</i>	1.727	0.3353	0.3354 0.3357 0.3358	752 004 931
35	<i>vw</i>	1.647	0.3686	0.3685 0.3686	392 4,10,0

Table 3 (cont.)

Number of lines (1)	Intensity* (2)	Spacing observed (3)	$Q(1/d_{hkl}^2)$		Indices (6)
			Observed (4)	Calculated (5)	
36	<i>vw</i>	1.628 Å	0.3773	0.3775 0.3779	0,11,0 234
37	<i>vw</i>	1.602	0.3897	0.3891 0.3896 0.3904	144 563; 4,10,1 733
38	<i>vw</i> (broad)	1.527	0.4289	0.4283 0.4286	11,0,0 663
39	<i>vw</i>	1.443	0.4802	0.4799	364
40	<i>vw</i>	1.382	0.5236	0.5234 0.5235	6,10,2 972

\* *vs*, very strong; *s*, strong; *m*, medium; *w*, weak; *vw*, very weak.

be 0.00354, 0.00312 and 0.02098 respectively. There is good agreement between the observed and calculated  $Q$  values as shown in Table 3. The unit-cell dimensions are:  $a=16.81$ ,  $b=17.90$ ,  $c=6.90_4$  Å. The density was measured with a specific-gravity bottle of very low weight, designed specially for the purpose, and is found to be  $1.27 \text{ g.cm}^{-3}$ . The density, calculated for eight molecules per unit-cell is  $1.30 \text{ g.cm}^{-3}$ . As can be seen from Table 3, systematic absences of the reflexions could not be assigned owing to the limited number of unresolved reflexions. The space group *Pmmm* is thus tentatively assigned to the crystal.

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#### References

- BERNAL, J. D. (1931). *Z. Kristallogr.* **78**, 363.  
 KHAWAS, B. & KRISHNA MURTI, G. S. R. (1968). *Indian J. Phys.* **42**, 175.  
 KRISHNA MURTI, G. S. R., NATARAJAN, R. & DEB, A. R. (1965). *Indian J. Phys.* **39**, 199.  
 LIPSON, H. (1949). *Acta Cryst.* **2**, 43.

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**The crystal structure of  $\text{Mg}_3\text{NF}_3$ .** By STEN ANDERSSON, *Research Institute of National Defence, FOA 4, Stockholm, Sweden*

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$\text{Mg}_3\text{NF}_3$  is cubic with  $a=4.216$  Å, space group *Pm3m*. The structure is related to the NaCl-structure type. The anion arrangement is ordered.

Two new nitride fluorides of magnesium are formed when nitrogen is passed over mixtures of Mg and  $\text{MgF}_2$  at temperatures of 900–1050°C. One of them,  $\text{Mg}_3\text{NF}_3$ , is cubic with  $a=4.216$  Å,  $D_m=3.16$ ,  $D_c=3.19 \text{ g.cm}^{-3}$  and  $Z=1$ . The space group is *Pm3m*, with three Mg atoms in the 3(*c*) positions, three F atoms in 3(*d*) and one N atom in 1(*b*).

The  $R$  value for 18 reflexions, collected with an X-ray powder diffractometer with Cu  $K\alpha$  radiation, was 0.022. The atomic form factors used were those for  $\text{Mg}^{2+}$ ,  $\text{F}^-$  and  $\text{N}^{3-}$  obtained from *International Tables for X-ray Crystallography* (1962); the  $\text{N}^{3-}$  form factors were constructed from the N and  $\text{N}^-$  curves given therein. If the anions were assumed to be randomly distributed over the 3(*d*) and 1(*b*) positions, the  $R$  value increased to 0.053.

A magnesium atom is octahedrally surrounded by four fluorine and two nitrogen atoms at equal distances of 2.108 Å. The nitrogen atom is octahedrally surrounded by six cations, as in  $\text{Ca}_2\text{N}$  (Keve & Skapski, 1968). A fluorine atom is surrounded by four cations in a square-planar arrangement. The structure of  $\text{Mg}_3\text{NF}_3$  is similar to the MgO or NaCl structure type, but with one of the cation positions (000) empty in an ordered way. The anion arrangement is intact, although the two different anions are ordered.

#### Reference

- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 KEVE, E. T. & SKAPSKI, A. C. (1968). *Inorg. Chem.* **7**, 1757.