Tabelle 8. *Abstände des* $H_2O(II)$ *zu seinen Nachbarn im* β-$KZnBr_3.2H_2O$ *und* $KZnJ.2H_2O$

	β-$KZnBr_3.2H_2O$	$KZnJ_3.2H_2O$	
H_2O (II)-X(1)	3,63 Å	3,84 Å	1. Basis des trigonalen Prismas
H_2O (II)-X(2)	3,54	3,77	
H_2O (II)-X(3)	3,65	3,82	
H_2O (II)-X(4)	3,64	3,87	2. Basis des trigonalen Prismas
H_2O (II)-X(5)	3,52	3,76	
H_2O (II)-X(6)	3,81	3,81	
H_2O (II)-X(7)	3,53	3,72	Pyramidenspitzen der Seitenflächen des Prismas
H_2O (II)-H_2O (I)	2,66	2,61	
H_2O (II)-K	2,78	2,81	

Die Anordnung der Nachbarn um das H_2O (II) ist entsprechend der um das Kalium.

Beide Strukturen lassen sich von einer verschiedenartig verzerrten hexagonal-dichtesten Brompackung ableiten. In beiden Fällen sind die Bromschichten sehr stark aufgeweitet und ineinanderverschachtelt (Fig. 3 und 4). Die Anordnung der so entstehenden Hohlkanäle ist in beiden Strukturen unterschiedlich; im α-$KZnBr_3.2H_2O$ verlaufen sie sämtlich in gleicher Orientierung, im β-$KZnBr_3.2H_2O$ sind sie jeweils um ihre Längsachsen gegeneinander verdreht.

Beide Strukturen haben das gleiche Volumen der Elementarzelle und in der Richtung der Hohlkanäle die gleiche Gitterkonstante. Die Atomabstände in beiden Modifikationen unterschieden sich nicht merklich. Auch der Schmelzpunkt ist etwa der gleiche.

Zwillingsbildung wurde beim β-$KZnBr_3.2H_2O$ nicht beobachtet, dagegen tritt α-$KZnBr_3.2H_2O$ nur in Zwillingsindividuen auf.

Beide Modifikationen von $KZnBr_3.2H_2O$ kristallisieren in verschiedenen Kristallklassen und unterscheiden sich wesentlich in ihrem Habitus. β-$KZnBr_3.2H_2O$ kristallisiert prismatisch, wobei die Prismenrichtung der kürzesten Translationsrichtung ($=c$) entspricht. α-$KZnBr_3.2H_2O$ bildet flache langgestreckte Scheiben mit der längsten Gitterkonstanten in Richtung der Längserstreckung.

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The Unit Cells and Space Groups of L-Methionine, L-β-Phenylalanine, and DL-Tyrosine

BY B. KHAWAS

Division of Agricultural Physics, Indian Agricultural Research Institute, New Delhi, 12, India

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The Debye–Scherrer patterns of L-methionine, L-β-phenylalanine and DL-tyrosine crystallized from aqueous solution, have been analysed. L-Methionine (2-amino-4-methylthiobutanoic acid), is monoclinic with $a=15{\cdot}49$, $b=3{\cdot}84$, $c=14{\cdot}11$ Å, $\beta=103°54'$; space group $P2_1$, $Z=4$. L-β-Phenylalanine is also monoclinic with $a=13{\cdot}13$, $b=6{\cdot}59_4$, $c=10{\cdot}28$ Å, $\beta=104°38'$; space group $P2_1$, $Z=4$. DL-Tyrosine (3-p-hydroxyphenylalanine) is orthorhombic with $a=21{\cdot}26$, $b=5{\cdot}85_2$, $c=13{\cdot}68$ Å,; space group $Pnc2$, $Z=8$.

Although the crystal structures of DL-methionine dimorphs (Mathieson, 1952) and the unit cells and space group of DL-β-phenylalanine (Khawas & Krishna Murti, 1968) and L-tyrosine (Khawas & Krishna Murti, 1969) have been reported, there appear to be no data on the crystal structure of L-methionine, L-β-phenylalanine, and DL-tyrosine. These compounds could not be obtained as good single crystals by the ordinary methods of crystallization; information regarding the structure was obtained from powder patterns alone. L-Methionine crystallized from aqueous or alcoholic solution at room temperature (25 °C–30 °C) does not show any dimorphism.

The patterns of the micro-crystals crushed to powder and rolled into the form of a cylinder (about 0·3 mm in diameter) with gum acaciae, were taken on an 11·48 cm diameter powder camera using Cu $K\alpha$-radiation. The positions of the lines were measured to an accuracy of 0·05 mm, and the spacings obtained were accurate to 0·001 Å for 2θ–62°. The d values were converted to Q ($10^4 . 1/d^2$), and a table of differences in Q values was prepared for each sample.

L-*Methionine*

Pure L-methionine, obtained from British Drug Houses Ltd, England, was crystallized from aqueous solution; the crystals are tiny, transparent and not very regular in shape. An application of the tests for higher symmetries (Ázároff & Buerger, 1958), on the experimental Q values from a powder photograph (Table 1) showed that the crystal system was not cubic, tetragonal, hexagonal, or orthorhombic. Ito's (1950) method was then tried using the general formula:

$$Q_{hkl}=h^2a^{*2}+k^2b^{*2}+l^2c^{*2}+2hka^*b^*\cos\gamma^* +2hl^*a^*c^*\cos\beta^*+2klb^*c^*\cos\alpha^* . \quad (1)$$

Table 1. *Powder pattern data of* L-*methionine*

		Q ($10^4.1/d^2$)		
Intensity	d	Observed	Calculated	hkl
vs	15·24 Å	43	44	100
vvw	13·60	54	52	001
w	7·628	172	177	200
vw	5·733	304	297	102
s	4·995	401	398	300
vw	4·769	440	441	$10\bar{3}$
vw	4·623	468	466	003
			467	$30\bar{2}$
			476	202
vs	4·449	505	505	$20\bar{3}$
s	4·366	525	519	301
s (bd.)	4·114	591	579	103
vs (bd.)	3·876	666	657	$30\bar{3}$
			667	$40\bar{1}$
w	3·693	733	730	$40\bar{2}$, 011
m	3·485	823	822	$20\bar{4}$
			829	004
m (bd.)	3·334	900	897	$40\bar{3}$
s	3·106	1037	1042	$50\bar{1}$
m	3·044	1079	1071	303
			1076	310
			1082	$50\bar{2}$
m (bd.)	2·880	1206	1197	311
s	2·730	1342	1335	$31\bar{3}$
			1345	$41\bar{1}$
			1348	$30\bar{5}$
m	2·655	1419	1421	312
s	2·578	1505	1500	$21\bar{4}$
			1503	304
			1505	$60\bar{1}$
			1507	014
m	2·508	1590	1591	600
vw	2·419	1709	1702	205
m	2·386	1757	1749	313
			1760	$51\bar{2}$
m (bd.)	2·318	1861	1865	006
			1868	214, $60\bar{4}$
vvw	2·222	2025	2020	$40\bar{6}$
			2026	$31\bar{5}$
m	2·149	2165	2163	$61\bar{1}$
			2166	700
w	2·080	2311	2318	206
w	2·023	2443	2449	$11\bar{6}$
vw	1·985	2538	2538	007
			2543	016
w (bd.)	1·921	2710	2712	020
w	1·796	3100	3093	$32\bar{1}$
			3099	$11\bar{7}$
w	1·757	3239	3231	321
vvw	1·693	3489	3493	223, $12\bar{4}$
w	1·650	3673	3677	124
vvw	1·595	3931	3936	$12\bar{5}$
vvw	1·550	4162	4166	125
vw	1·519	4334	4329	10, 0, $\bar{4}$
vvw	1·486	4529	4537	$52\bar{5}$
vvw	1·445	4785	4787	209
vvw	1·403	5080	5072	814
			5087	10, 0, 2

Assuming the first two lines to have indices 100 and 001, $Q_{100}=44·2$ and $Q_{001}=51·8$ were computed respectively from the observed pairs $Q_{600}=1591$, $Q_{700}=2165$ and $Q_{006}=1861$, $Q_{007}=2538$. With these values of Q_{100} and Q_{001} on substitution in formula (1), other pinacoidal reflexions for $h=2$, 3 and $l=3$, 4 could be found. If the third line is assumed to be the second order of the first, and the 4th line to have index 102, the above formula gave $2hla^*c^*\cos\beta^*=23$ computed from observed $Q_{20\bar{4}}=823$. Taking these three parameters the first 16 lines and a few of the rest could be indexed for $h0l$ zone. Next $Q_{010}=678$ was computed from $Q_{020}=2710$, so that from $Q_{50\bar{2}}=1079$, the 23rd line could be indexed as $51\bar{2}$ for $Q_{\rm obs}=Q_{\rm calc}=1757$, giving $\alpha^*=90=\gamma^*$ from the above formula. All the lines in the pattern were now indexed, using these 6 constants, within the discrepancy $|Q_{\rm obs}-Q_{\rm calc}|=8$, for sharp lines; the following constants followed for the reciprocal unit cell $a^*=0·0648$, $b^*=0·2598$, $c^*=0·07198$ Å, $\beta^*=76°6'$.

De Wolff (1968) has propounded a simplified criterion for the reliability of an indexed pattern, in the form of a figure of merit, defined by

$$M_{20}=Q_{20}/2\bar{\varepsilon}N_{20} \quad (2)$$

where Q_{20} = the Q value for 20th observed and indexed line,
N_{20} = the number of different Q values calculated up to Q_{20}
$\bar{\varepsilon}$ = the average discrepancy in Q for these 20 lines.

This should have a value greater than 10 for correct indexing of a powder pattern. For L-methionine (Table 1), $Q_{20}=1505$, $N_{20}=31$, and $\bar{\varepsilon}=3·3$, so $M_{20}=7·30$.

Thus the indexing of the pattern of L-methionine can be taken as correct.

The direct cell derived from the above reciprocal parameters has: $a=15{\cdot}49, b=3{\cdot}84, c=14{\cdot}11$ Å, $\beta=103°54'$; which Buerger's (1957) test shows to be the reduced cell. The observed density 1·22 g.cm^{-3}, measured to an accuracy of 0·005 g.cm^{-3} gave the number of molecules per unit cell as 4·0. The lines in the pattern were given all possible indices, within the above discrepancy, and the following conditions limiting possible reflexions were found:

hkl, no condition
*h*0*l*, no condition .

0*k*0, $k=2$n (only three orders were in the range of observation). The probable space group is thus $P2_1$ or $P2_1/m$, the former being chosen for an optically active molecule, which is asymmetric.

L-*β*-*Phenylalanine*

Pure L-*β*-phenylalanine, obtained from British Drug Houses Ltd, England, was crystallized from aqueous solution by repeated evaporation at room temperature. X-ray patterns of the powdered microcrystalline mass were taken. Tests for the higher symmetries (Azároff & Buerger, 1958) over the observed Q values (Table 2) for a cubic, tetragonal, hexagonal or an orthorhombic cell were negative. The pattern could be analysed satisfactorily by Ito's (1950) method for a monoclinic cell as described earlier in the case of L-methionine. The first three lines were given indices 100, 001, and $10\bar{1}$ and $Q_{100}=62$, $Q_{001}=101$ could be computed from observed $Q_{400}=991$, $Q_{600}=2238$, and $Q_{30\bar{2}}=722$, $Q_{20\bar{4}}=1543$, giving the factor $2a^*c^*\cos\beta^*=40$. With these three constants, using formula (1), the 4th, 5th and 6th line were identified as 101, 200, and $20\bar{1}$. Next $Q_{010}=230$ was taken from observed $Q_{41\bar{3}}=1650$, $Q_{031}=2171$, giving $\alpha^*=90°=\gamma^*$. The reciprocal cell constants, derived from the above six parameters are: $a^*=0{\cdot}07874$, $b^*=0{\cdot}1517$, $c^*=0{\cdot}1005$ Å, $\beta^*=75°22'$ with which all the lines in the pattern could be indexed satisfactorily, within discrepancy $|Q_{\rm obs}-Q_{\rm calc}|=8$, except the third and seventh line, which had discrepancies 10 and 12 respectively.

Following de Wolff (1968), from Table 2, $Q_{20}=1209$, $X_{20}=1$, $N_{20}=21$; $\bar{\varepsilon}=4{\cdot}25$ and M_{20} calculated from formula (2) is 6·76. The indexing of the pattern of L-*β*-phenylalanine is thus correct. The direct cell dimensions are $a=13{\cdot}13$, $b=6{\cdot}59_4$, $c=10{\cdot}28$ Å, $\beta=104°38'$, which after Buerger's (1957) method are found reduced and correspond to the primitive unit cell. The observed density is 1·28 g.cm^{-3} and density calculated for $Z=4$, is 1·27 g.cm^{-3}.

The lines in the pattern were given all possible indices (Table 2) within the above discrepancy and the conditions limiting possible reflexions are:

hkl, no condition
*h*0*l*, no condition

0*k*0, $k=2n$ (only three orders were in the range of observation). The probable space group is $P2_1$ or $P2_1/m$. The former is assigned for the same reason as for L-methionine.

Table 2. *Powder pattern data of* L-*β*-*phenylalanine*

		Q ($10^4.1/d^2$)		
Intensity	*d*	Observed	Calculated	*hkl*
vs	13·60 Å	54	62	100
s	10·35	93	101	001
m	8·672	133	123	$10\bar{1}$
m	6·972	206	203	101
vs	6·414	243	248	200
m	6·027	275	269	$20\bar{1}$
vw	5·733	304	292 (?)	110 (?)
s	5·451	336	331	011
vs	5·111	383	386	$10\bar{2}$
s	4·598	473	478	210
vs	4·323	535	539	$30\bar{1}$
w	4·218	562	558	300
s	4·023	618	616	$11\bar{2}$
s	3·900	657	659	211
vw (bd.)	3·722	722	722	$21\bar{2}$, $30\bar{2}$
s	3·514	810	812	202
vs	3·433	849	851	$10\bar{3}$
s	3·296	927	920	$40\bar{1}$
			933	020
vw	3·177	991	992	400
vw	2·950	1149	1147	$21\bar{3}$
w	2·876	1209	1202	302
vvw	2·827	1251	1253	401
vs	2·750	1322	1324	022
w	2·683	1389	1397	203
vw	2·632	1444	1451	$50\bar{1}$
w	2·546	1543	1542	$20\bar{4}$
			1550	500
vw	2·462	1650	1642	$32\bar{2}$
			1651	$41\bar{3}$
m	2·344	1820	1827	303
w	2·265	1949	1946	412
m	2·146	2171	2171	031
vw	2·114	2238	2232	600
vvw	2·006	2485	2483	$30\bar{5}$
vvw	1·971	2574	2573	601
vvw	1·943	2649	2654	304
vw	1·908	2741	2747	323
vw	1·831	2983	2979	033
vvw	1·782	3149	3152	620
vvw	1·754	3250	3248	404

DL-*Tyrosine*

Pure DL-tyrosine was obtained from Sigma Chemical Co., St. Louis, U.S.A. It crystallizes from aqueous solution in very fine short needles, unlike L-tyrosine where these needles were longer and a fibre diagram (Khawas & Krishna Murti, 1969) about the needle axis could be taken. X-ray patterns of the powdered crystals were taken. An application of the tests of higher symmetries (Azároff & Buerger, 1958) to the observed Q values (Table 3) showed that the crystal system was not cubic, tetragonal, or hexagonal but a number of constant ΔQ values were observed, which suggested that crystal system might be orthorhombic. The Q values were multiplied by $\lambda^2/4$ to get corresponding $\sin^2\theta$ values (Table 3), and the pattern was analysed by Lipson's (1949) method, giving the following constants for a satisfactory indexing of all observed lines, where $\lambda = 1\cdot5418$ Å.

$$\sin^2\theta_{100} = 13\cdot14$$
$$\sin^2\theta_{010} = 173\cdot6$$
$$\sin^2\theta_{001} = 31\cdot8$$

Table 3. *Powder pattern data of* DL-*tyrosine*

		$10^4 \sin^2\theta$		
Intensity	d	Observed	Calculated	*hkl*
vw	10·60 Å	53	53	200
s	6·510	140	140	102
vs	5·733	181	180	202
s	5·294	212	210	400
vs	4·893	248	245	302
vs	4·473	297	292	310
vs	4·124	349	353	212
s	3·917	387	384	410
m	3·761	419	416	411
			420	312
vs	3·576	465	460	013
vs	3·408	512	509	004
			511	412
			512	213
vs	3·243	565	561	204
vs (bd.)	3·084	625	627	304
			629	512
vs	2·927	694	694	020
			696	114
m	2·849	732	735	214
vs	2·730	797	801	314
s	2·639	853	849	711
w	2·578	894	893	414
m	2·528	930	932	613
m	2·442	996	994	123
s	2·407	1027	1021	215
			1023	520
s (bd.)	2·254	1169	1166	620
m	2·189	1241	1238	910
m	2·126	1314	1314	10, 0, 0
s	2·091	1359	1355	406
			1365	912
m	2·034	1436	1436	316
			1441	615; 10, 0, 2
s	1·977	1521	1519	10, 1, 1
			1523	814
w	1·937	1584	1590	11, 0, 0
s	1·893	1659	1663	822
w	1·863	1712	1712	331
			1717	11, 2, 0
vw	1·824	1786	1784	217
			1789	706
			1790	616; 921
vw	1·777	1882	1886	922
vvw	1·749	1943	1943	417
vw	1·708	2037	2035	008
			2034	630
vw	1·684	2095	2098	12, 1, 1
			2099	11, 0, 4
s	1·660	2157	2153	308
			2159	816
s	1·625	2251	2245	408
m	1·599	2325	2327	328
			2330	825
vvw	1·569	2414	2410	235
			2412	418; 11, 2, 2
w	1·546	2486	2483	726
vvw	1·530	2539	2536	518
			2543	634
m	1·483	2702	2703	14, 0, 2
m	1·456	2803	2802	219
			2803	10, 2, 5
vw	1·430	2906	2903	926; 13, 1, 4
			2905	042
			2908	11, 1, 6
			2912	834
vw	1·418	2956	2956	15, 0, 0
			2957	242
			2960	419
vw	1·380	3121	3116	243
			3121	037
vw	1·329	3365	3364	16, 0, 0
			3365	13, 0, 6
w	1·308	3473	3472	3, 1, 10
w	1·287	3588	3588	145
			3590	819
			3593	637

To apply de Wolff's (1968) test, we can write

$(\sin^2\theta)_{20} = 996$, the $\sin^2\theta$ value for 20th observed and indexed line,

$N_{20} = 25$, the number of different $\sin^2\theta$ values calculated up to $(\sin^2\theta)_{20}$

$\tilde{\varepsilon} = 2\cdot3$, the average discrepancy in $\sin^2\theta$ values,

and $M_{20} = 8\cdot70$ calculated from formula (2).

This shows that the indexing is substantially correct. The unit cell derived has $a = 21\cdot26$, $b = 5\cdot852$, $c = 13\cdot68$ Å. Assuming $Z = 8$, the density calculated is 1·41 g.cm^{-3} and observed density is 1·37 g.cm^{-3}.

All the possible indices for each observed line within a discrepancy of $|\sin^2\theta_{\text{obs}} - \sin^2\theta_{\text{calc}}| = 6$, were given. the conditions limiting possible reflexions from Table 3 are:

hkl, no condition
h0l, $1 = 2n$
0kl, $k + l = 2n$
hk0, no condition.

The probable space group is *Pnc*2 or *Pncm*. The former is assigned for an organic molecule.

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