

present; it is occupied only on a statistical basis (occupancy of 22%) by sodium atoms. This cation could be said to be attached to the cavity wall, while the surface still exposed is coordinated by water molecules. This type of coordination is usual in zeolites and has been found, for instance in harmotome (Sadanaga, Marumo & Takéuchi, 1961), jugawaralite, and has also been noted in gismondite and levinite (Kerr & Williams, 1969).

Note added in proof: Since the acceptance of this paper another study on the refinement of stilbite has been published (Slaughter, 1970). Differences between the two papers are slight: Slaughter examines cation positions < 5% occupancy; he suggests a different interpretation of the distribution of Si/Al atoms; temperature factors are slightly different.

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The Crystal Structure of L-Dopa Hydrochloride, 3-(3,4-Dihydroxyphenyl)-L-Alanine Hydrochloride, C₉H₁₂O₄NCl*

BY RONALD J. JANDACEK AND KENNETH M. EARLE

Neuropathology Branch, Armed Forces Institute of Pathology, Washington, D.C. 20305, U.S.A.

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The crystal structure of L-dopa hydrochloride, 3-(3,4-dihydroxyphenyl)-L-alanine hydrochloride, was determined from three-dimensional data collected manually with a General Electric XRD6 diffractometer using Cu $K\alpha$ radiation. The crystals are monoclinic, $P2_1$, with $a = 6.261 \pm 0.007$, $b = 5.821 \pm 0.001$, $c = 15.646 \pm 0.003$ Å, and $\beta = 112.66 \pm 0.02^\circ$. The structure was refined to a conventional R value of 7.9%. Extensive intermolecular hydrogen bonding is present. The aromatic ring forms an angle of 39.1° with the plane of the carboxyl group.

The compound 3-(3,4-dihydroxyphenyl)-L-alanine (L-dopa) (Fig. 1) has been used for the treatment of Parkinson's disease. Slowly increasing oral doses of L-dopa have been reported to induce at least partial improvement of some of the manifestations of Parkinson's disease, and in some cases the improvement has been

dramatic (Cotzias, Papvasiliou & Gellene, 1969). Because of the interest in this compound as a promising therapeutic agent, the study of the crystal structure of the hydrochloride of this amino acid was undertaken.

Experimental

Crystals of the hydrochloride of L-dopa were obtained by the evaporation of a solution of L-dopa in concentrated hydrochloric acid. The L-dopa was obtained from Nutritional Biochemicals Corporation. The crystal was aligned with the unique b axis parallel to the φ axis of a General Electric XRD6 diffractometer single-crystal orienter. The space group was determined to be $P2_1$ by searching for reflections with the diffracto-

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Reprint requests to the Armed Forces Institute of Pathology, Washington, D.C. 20305 (Dr Earle).

meter. The following dimensions of the unit cell were determined by a least-squares fit to 2θ values measured with Cu $K\alpha$ radiation and the diffractometer with a 0.02° slit in the receiving aperture:

$$a = 6.261 \pm 0.002 \text{ \AA}, \quad b = 5.821 \pm 0.001, \\ c = 15.646 \pm 0.003 \text{ \AA}, \quad \beta = 112.66 \pm 0.02^\circ.$$

There are two formula weights in the unit cell, and the calculated density is 1.478 g.cm^{-3} as compared with 1.477 g.cm^{-3} , measured by flotation in carbon tetrachloride and benzene.

The data were measured by the stationary-counter stationary-crystal technique with Ni-filtered Cu $K\alpha$ radiation, and 880 of 903 independent intensities were considered observed. The unobserved reflections were assigned intensities equal to 0.5 times the intensity of the minimum observable intensity. The intensity data were converted to structure amplitudes by the application of Lorentz and polarization factors, a factor to correct for $\alpha_1\alpha_2$ splitting, and a factor to approximately correct absorption as a function of the diffractometer ϕ setting.

Determination of the structure

The x and z coordinates of the chloride ion were determined from a three-dimensional Patterson func-

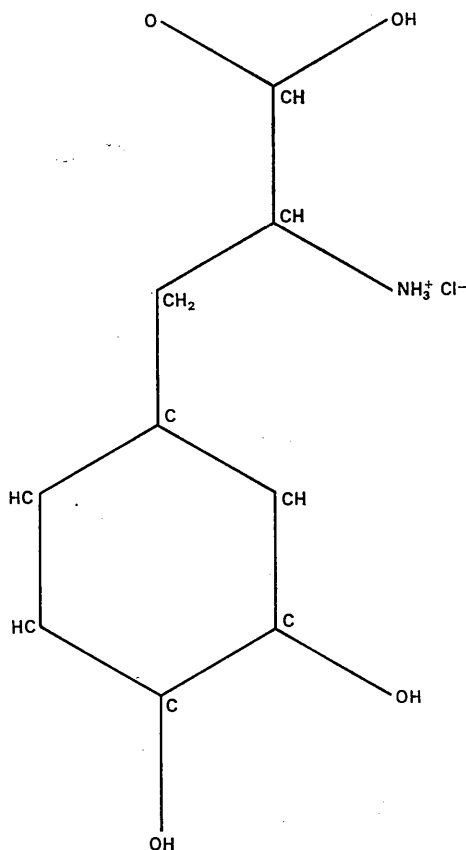


Fig. 1. Structural formula of L-dopa.HCl.

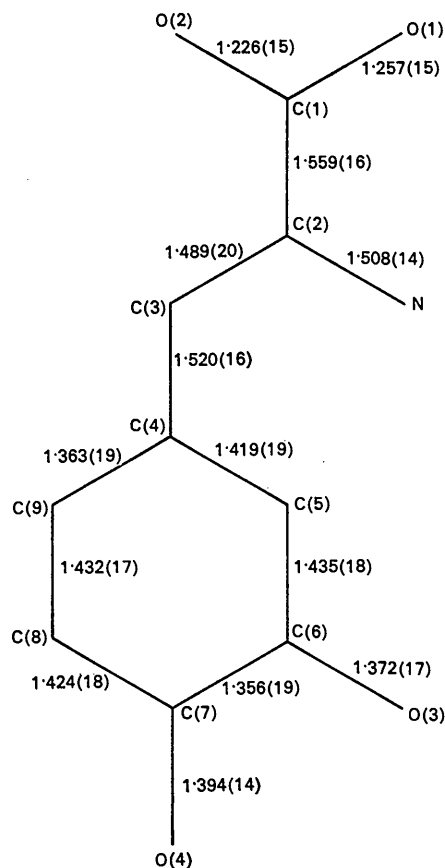


Fig. 2. Bond distances with e.s.d.'s $\times 10^3$ in parentheses.

tion, and an arbitrary y coordinate was assigned. A three-dimensional Fourier synthesis was calculated with the phases determined by the chloride position. The spurious mirror plane in this map did not prevent the correct determination of the positions of all non-hydrogen atoms of the molecule.

Table 1. Atomic positions

E.s.d.'s $\times 10^4$ are given in parentheses.

	x/a	y/b	z/c
Cl ⁻	0.4075 (4)	0.4118	0.0587 (2)
N	0.4707 (13)	0.4150 (26)	0.8683 (6)
C(1)	0.8470 (18)	0.4658 (23)	0.8529 (8)
C(2)	0.5808 (17)	0.4412 (31)	0.7986 (7)
C(3)	0.5269 (18)	0.2407 (28)	0.7348 (8)
C(4)	0.2693 (18)	0.2163 (25)	0.6781 (7)
C(5)	0.1506 (19)	0.0269 (25)	0.6962 (8)
C(6)	0.0912 (21)	0.0033 (25)	0.6401 (8)
C(7)	0.1997 (18)	0.1595 (25)	0.5732 (8)
C(8)	0.0835 (19)	0.3521 (23)	0.5552 (8)
C(9)	0.1576 (19)	0.3741 (28)	0.6115 (8)
O(1)	0.9135 (12)	0.4117 (27)	0.9369 (5)
O(2)	0.9642 (13)	0.5279 (21)	0.8100 (6)
O(3)	0.2206 (14)	0.1750 (19)	0.6518 (7)
O(4)	0.4332 (12)	0.1204 (18)	0.5205 (6)

After four molecules of full-matrix least-squares refinement with isotropic temperature factors, the R

index ($\sum||F_o| - |F_c|| / (\sum|F_o|)$) was 12.8%. Three cycles of least-squares with anisotropic temperature factors reduced the R to 8.8%, and a difference density was then calculated. The hydrogen atoms were identified in this map and were included in three cycles of full-matrix least-squares with isotropic temperature factors of 2.0 \AA^2 . All hydrogen parameters were held constant, and all reflections were weighted equally; the final R value is 7.9%. The scattering factors used are those found in *International Tables for X-ray Crystallo-*

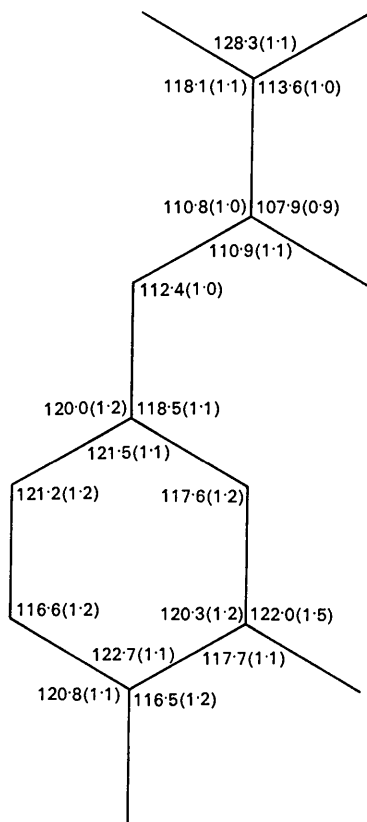


Fig. 3. Bond angles in degrees with e.s.d.'s in parentheses.

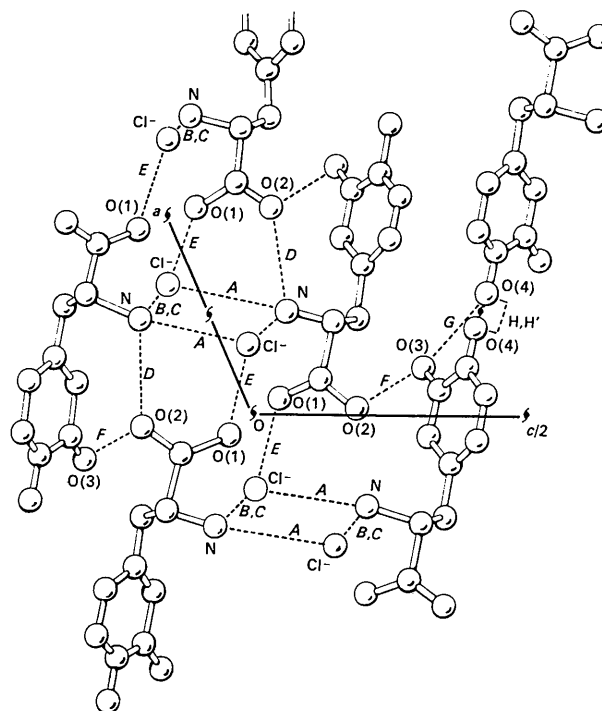


Fig. 4. A projection along the b axis. The broken lines indicate probable hydrogen bonds identified by labels A through H , which are described in Table 4.

graphy (1962). The fractional coordinates of the atoms are given in Table 1, and anisotropic temperature factors are listed in Table 2. Table 3 lists the observed and calculated structure amplitudes and the phase angles, with unobserved reflections followed by 'U'.

Discussion of the structure

The bond lengths and angles are shown in Fig. 2 and 3 respectively. The aromatic ring is planar, with all six of the carbon atoms less than 0.01 \AA from the best-fit plane of the ring. C(3) and O(4) are 0.04 \AA from this plane, and O(3) is less than 0.01 \AA from it. The four

Table 2. Anisotropic temperature factors $\times 10^3$

The form of the expression is $\exp[-\{h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}\}]$. E.s.d.'s range from 0.1×10^{-4} to 6×10^{-3} .

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl ⁻	12.8	11.2	2.9	0.5	1.5	0.0
N	9.4	17.6	2.6	-2.3	3.1	-1.1
C(1)	8.1	17.3	2.8	2.2	1.1	-0.7
C(2)	6.8	21.9	2.7	-2.2	2.7	-0.9
C(3)	6.2	28.2	2.2	-1.8	0.9	-4.0
C(4)	7.4	20.6	1.9	3.0	0.9	-0.5
C(5)	11.1	17.6	2.6	3.5	1.3	0.3
C(6)	14.4	13.6	2.6	-0.3	2.5	-2.3
C(7)	7.4	17.7	2.4	1.1	0.7	-1.8
C(8)	11.3	19.6	2.7	-0.7	1.7	0.5
C(9)	11.1	22.3	2.7	-5.7	1.7	-0.9
O(1)	6.9	35.6	3.0	-4.4	0.7	1.6
O(2)	6.6	37.8	4.2	0.1	3.2	4.2
O(3)	10.5	16.6	5.3	-1.5	2.6	1.7
O(4)	7.1	21.0	3.7	-0.3	0.9	0.9

Table 3 (cont.)

$\sum 10 F_{0l} 10 F_{cl} \text{ } \alpha^\circ$				$\sum 10 F_{0l} 10 F_{cl} \text{ } \alpha^\circ$				$\sum 10 F_{0l} 10 F_{cl} \text{ } \alpha^\circ$				$\sum 10 F_{0l} 10 F_{cl} \text{ } \alpha^\circ$				$\sum 10 F_{0l} 10 F_{cl} \text{ } \alpha^\circ$							
45E				46E				51E				53E				60E				63E			
-4	82	86	168	0	26	31	357	-3	171	163	85	-5	95	98	15	0	130	146	180	-8	54	55	299
-3	56	60	113					-2	80	83	25	-4	161	158	31	1	114	124	180	-7	36	47	345
-2	75	69	98					-1	38	41	43	-3	207	208	330	2	95	105	180	-6	43	52	155
-1	169	165	6	-18	37	29	0	0	57	50	286	-2	137	142	18	5	91	97	180	-5	61	62	79
0	207	202	301	-17	68	67	0	1	121	119	190	-1	99	97	222	4	48	54	180	-4	109	114	175
1	186	195	72	-16	10	7	180 U	-2	90	91	268	0	24	16	282	5	46	58	0	-3	61	75	181
2	181	167	312	-15	10	3	0	3	161	171	244	1	108	109	163	2	81	88	205	-2	67	71	204
3	187	188	154	-14	19	19	180	4	101	104	237	2	91	88	205	0	34	38	116	0	34	38	116
4	67	95	60	-13	47	52	180	5	42	40	237	3	91	95	177	-13	56	59	353				
5	23	22	220	-12	38	31	0	6	86	84	210					-12	37	43	78				
6	51	54	171	-11	10	2	0									-11	77	81	108	0	76	91	44
7	23	25	137	-10	133	136	180	-15	9	17	319 U	-10	66	74	44	-10	159	116	59				
				-9	138	132	180	-14	39	38	188	-9	57	62	67	-9	91	97	287				
				-8	186	188	180	-13	22	26	76	-8	92	94	72	-8	89	94	156	-14	15	20	180
				-7	55	54	180	-12	15	17	140	-7	54	61	53	-7	112	119	355	-13	158	183	0
				-6	126	115	0	-11	73	76	63	-6	15	11	68	-6	98	95	179	-11	63	53	180
				-5	193	196	0	-10	91	88	60	-5	100	103	275	-5	62	66	73	-10	68	82	0
				-4	25	18	0	-9	196	203	143	-4	36	44	273	-4	102	102	209	-9	92	105	180
				-3	9	6	180 U	-8	128	139	158	-3	128	129	173	-3	166	171	257	-8	19	25	180
				-2	15	7	180 U	-7	156	155	60	-2	72	76	266	-2	47	53	260	-7	37	34	180
				-1	153	155	0	-6	113	118	241	-1	21	11	61	-1	65	56	235	-6	14	17	180
				0	101	97	0	-5	37	36	277	0	95	97	208	0	24	29	188	-5	57	61	180
				1	22	22	180	-4	117	114	331	1	32	33	164	1	29	27	65	-4	53	64	180
				2	116	114	0	-3	154	163	248					2	26	23	11	-3	119	150	180
				3	28	22	180	-2	63	89	115					3	41	43	180	-2	41	43	180
				4	24	17	0	-1	143	141	312					4	39	39	0	-1	23	25	0
				5	46	46	180	0	54	46	328	-17	23	21	180	-12	39	44	43	-1	23	25	0
				6	76	85	180	1	95	78	286	-16	60	65	180	-11	14	11	334	0	36	53	0
				7	110	136	180	2	23	25	262	-15	95	121	180	-10	48	61	261	1	37	39	0
				8	46	49	180	3	20	47	269	-14	74	86	180	-9	102	111	287				
								4	52	61	55	-13	17	16	180 U	-8	131	151	289				
								5	24	27	138	-12	17	16	180 U	-7	108	120	318	0	47	55	0
												-11	17	9	180 U	-5	17	10	63 U				
												-10	157	162	0	-4	42	52	210				
												-9	52	24	180 U	-3	64	61	162	0	50	65	4
												-8	140	160	0	-2	36	35	78				
												-7	86	67	0	-1	71	76	100				
												-6	95	19	180	0	86	61	111				
												-5	14	19	180	1	116	124	117				
												-4	34	38	180								
												-3	10	7	0 U								
												-2	121	134	180 U								
												-1	42	39	0	-9	23	20	19				

Table 4. Description of probable hydrogen bonding shown in Fig. 4

Molecules I and II are the (xyz) and $(\bar{x}, \frac{1}{2} + y, \bar{z})$ molecules.
E.s.d.'s in distance are from 0.010 to 0.015.

Type of interaction shown in Fig. 4	Probable donor (molecule I, 000)	Acceptor	Acceptor molecule	Acceptor translation	Distance
A	N	Cl ⁻	I	(001)	3.16 Å
B	N	Cl ⁻	II	(101)	3.10
C	N	Cl ⁻	II	(111)	3.13
D	N	O(2)	I	(100)	3.02
E	O(1)	Cl ⁻	I	(101)	2.94
F	O(3)	O(2)	I	(110)	2.87
G	O(4)	O(3)	II	(101)	2.98
H	O(4)	O(4)	II	(101)	3.03
H'	O(4)	O(4)	II	(111)	3.03

the type A Cl-N interaction may be only the result of ionic attraction. The intermolecular interactions of the hydroxyl groups bonded to the phenyl group (types G, H, and H') are exceptionally long for oxygen to oxygen-hydrogen bonding (2.98 and 3.03 Å). The position of the peak in the difference density corresponding to the hydrogen bonded to O(4) indicates that it is attracted to both O(4) and O(3) of the molecule related by the screw axis, and again a bifurcated system is indicated. It should be noted that the intermolecular distances identified as H and H' are the same type of interaction, but for a given molecule O(4) acts as a

donor in type H and an acceptor in type H' in the probable hydrogen-bonding system mentioned above.

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