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## The Crystal and Molecular Structure of DL-*p*-Nitrophenylalanine Hydrochloride\*

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$C_9H_{10}N_2O_4 \cdot HCl$  crystallizes in the space group  $P2_1ab$  with  $a = 28.753$  (15),  $b = 14.492$  (6),  $c = 5.313$  (5) Å,  $Z = 8$ . Data for 1647 reflections were collected on a Picker diffractometer. The structure was solved by packing considerations and refined to a final  $R$  of 0.05. The crystal structure has two molecules per asymmetric unit and has an interesting, nearly perfect, non-crystallographic centre of symmetry which relates the L and D molecules in the asymmetric unit. The crystal structure is stabilized by a network of N–H...Cl, O–H...Cl and C–H...O hydrogen bonds.

### Introduction

Crystal structure analyses of amino-acid antagonists have been recently started in this laboratory. Here we present the structure of the hydrochloride derivative of *p*-nitrophenylalanine (PNPA.HCl) which is an antagonist of phenylalanine and tyrosine. The effect of PNPA has been studied on *Escherichia coli* and its aromatic amino-acid-requiring mutants by Bergman, Sicher & Volcani (1953) and it has been found that PNPA interferes with the utilization of tyrosine in these systems.

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### Experimental

PNPA was obtained from the Sigma Chemical Co. (USA) and well formed needles were grown from dilute hydrochloric acid. A crystal  $0.2 \times 0.2 \times 0.3$  mm was mounted on a Picker FACS-1 diffractometer such that  $c$  coincided with the  $\varphi$  axis of the diffractometer. Cell dimensions were determined by a least-squares fit to the settings of 25 reflections. Crystal data are:  $C_9H_{10}N_2O_4 \cdot HCl$ , FW 246.65, orthorhombic,  $P2_1ab$ ,  $Z = 8$ ,  $a = 28.753$  (15),  $b = 14.492$  (6),  $c = 5.313$  (5) Å,  $D_m = 1.475$ ,  $D_c = 1.480$  g cm<sup>-3</sup>,  $\mu = 30.8$  cm<sup>-1</sup>,  $\lambda(Cu K\alpha) = 1.5418$  Å.

Intensities of 1647 unique reflections with  $2\theta \leq 130^\circ$  were measured. The  $\theta$ – $2\theta$  scan technique was em-

ployed with a  $2^\circ \text{ min}^{-1}$  scan speed. The scan range was  $2^\circ$  and background was measured on either side of the peak for 10 s. Intensities  $< 2\sigma(I)$  were considered unobserved and were excluded. The data were corrected for Lorentz and polarization factors but not for absorption.

### Structure determination and refinement

The cell dimensions are closely related to those of L-phenylalanine hydrochloride (PA.HCl) (Gurskaya, 1965). A neutron diffraction study of PA.HCl has been reported (Al-Karaghoulis & Koetzle, 1975). The cell dimensions from the neutron diffraction study of PA.HCl [ $a = 27.763(17)$ ,  $b = 7.059(4)$ ,  $c = 5.380(5)$  Å] indicate that  $a$  and  $c$  are nearly the same as in PNPA.HCl while  $b$  of PNPA.HCl is nearly twice that of PA.HCl. However, PA.HCl crystallizes in space group  $P2_12_12_1$ . Apart from the systematic absences ( $h0l$ ,  $h$  odd, and  $hk0$ ,  $k$  odd) of space group  $P2_1ab$ , photographs indicated additional absences. (The photographs showed that  $00l$  reflections for  $l$  odd were absent, and that for  $0k0$  only those reflections of the type  $k = 4n$  were present.) These factors and the doubling of  $b$  for PNPA.HCl strongly indicated that there should be similar packing features between the two structures even though the space groups are different. With the coordinates of PA.HCl (Gurskaya, 1965) and stereochemical fitting of the nitro group, the structure was initially packed in  $P2_12_12_1$  which gave a short contact of about  $2.6$  Å between C(5) of the aromatic ring and the  $c$ -screw-related O(3). However, instead of the screw-related molecule, if we consider a D molecule related by a non-crystallographic centre of symmetry to the L molecule, the short contact is relieved and the structure can be well packed assuming the correct space group  $P2_1ab$ , with two molecules (L

and D) in the asymmetric unit and with the necessary translation of molecules with respect to  $b$ . All the hydrogen bonds observed in PA.HCl (Al-Karaghoulis & Koetzle, 1975) could be satisfied for this structure. The initial structure factor calculation with two molecules in the asymmetric unit (related by a non-crystallographic centre of symmetry) gave an  $R$  of 0.40. The structure factors also satisfied the additional absences. The non-hydrogen atoms were successfully refined by full-matrix least squares (Gantzel, Sparks & Trueblood, 1961) to an  $R$  of 0.12. Because of the two molecules in the asymmetric unit, only partial refinement was carried out for the structure, first by refining the L and then the D molecule in stages. A difference synthesis at  $R = 0.12$  gave peaks at all the expected H positions. H atoms were included but were not refined. Anisotropic temperature factors were applied for all the non-hydrogen atoms and the structure was again refined to a final  $R$  of 0.050. Hughes's (1941) weights were used ( $1/w^2$  where  $w = |F_o|$  for  $|F_o| \geq 15.0$  and  $w = 15.0$  for  $|F_o| < 15.0$ ). Scattering factors were those listed in *International Tables for X-ray Crystallography* (1962) and a  $\Delta f'$  correction ( $= 0.3$ ) was applied to Cl<sup>-</sup>. Tables 1 and 2 give the final coordinates.\*

### Results and discussion

The coordinates given in Table 1 show the packing similarity of PNPA.HCl to that of PA.HCl. One can find the approximate relation between these structures by noting that the  $x$  and  $z$  coordinates of this structure (of the unprimed atoms of the L molecule) agree closely

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33153 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Final positional parameters ( $\times 10^4$ ) of the non-hydrogen atoms

	$x$	$y$	$z$		$x$	$y$	$z$
C(1)	661 (2)	2357 (4)	3115 (11)	C(1')	4334 (2)	135 (3)	1895 (11)
C(2)	693 (2)	1748 (4)	5448 (11)	C(2')	4308 (2)	754 (4)	-416 (10)
C(3)	1187 (2)	1512 (4)	6290 (11)	C(3')	3811 (2)	981 (4)	-1250 (10)
C(4)	1474 (2)	1002 (4)	4350 (11)	C(4')	3529 (2)	1509 (4)	659 (10)
C(5)	1753 (2)	1462 (4)	2647 (13)	C(5')	3248 (2)	1055 (4)	2396 (13)
C(6)	2014 (2)	978 (4)	850 (13)	C(6')	2987 (2)	1529 (4)	4164 (12)
C(7)	1982 (2)	32 (4)	832 (13)	C(7')	3021 (2)	2483 (4)	4187 (11)
C(8)	1711 (2)	-451 (4)	2505 (13)	C(8')	3284 (2)	2966 (4)	2520 (13)
C(9)	1462 (2)	37 (4)	4312 (13)	C(9')	3534 (2)	2463 (4)	723 (12)
N(1)	406 (2)	906 (4)	4964 (9)	N(1')	4592 (2)	1582 (4)	115 (8)
N(2)	2249 (2)	-477 (4)	-1048 (11)	N(2')	2748 (2)	2978 (4)	6104 (10)
O(1)	460 (2)	2150 (3)	1240 (8)	O(1')	4534 (2)	337 (3)	3814 (7)
O(2)	882 (2)	3141 (4)	3477 (11)	O(2')	4115 (2)	-651 (3)	1510 (10)
O(3)	2591 (2)	-94 (4)	-1984 (11)	O(3')	2410 (2)	2602 (4)	7011 (10)
O(4)	2121 (2)	-1243 (4)	-1638 (11)	O(4')	2876 (2)	3753 (3)	6680 (10)
Cl	518 (0)	-352 (1)	-58 (3)	Cl'	4482 (0)	2845 (1)	5216 (3)

Table 2. Positional parameters of the hydrogen atoms ( $\times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
H(1)N(1)	50	60	360	2.84	H(1')N(1')	450	190	140	2.84
H(2)N(1)	50	50	644	2.84	H(2')N(1')	450	200	-144	2.84
H(3)N(1)	12	106	478	2.84	H(3')N(1')	488	144	22	2.84
H(4)O(2)	89	363	200	4.87	H(4')O(2')	411	-113	300	4.87
H(5)C(2)	52	212	699	2.65	H(5')C(2')	448	38	-199	2.65
H(6)C(3)	136	215	675	3.29	H(6')C(3')	364	35	-175	3.29
H(7)C(3)	116	108	795	3.29	H(7')C(3')	384	142	-295	3.29
H(8)C(5)	177	219	269	3.48	H(8')C(5')	323	31	231	3.45
H(9)C(6)	222	134	-51	3.83	H(9')C(6')	278	116	551	3.83
H(10)C(8)	169	-120	238	3.66	H(10')C(8')	331	370	262	3.66
H(11)C(9)	125	-34	567	3.30	H(11')C(9')	375	284	-67	3.30

with those of PA.HCl (except for the nitro group). The *y* coordinates of the L molecule are nearly ( $y/2 - \frac{1}{8}$ ) those of PA.HCl. (This is because *b* is nearly doubled in the present case and the origin along *b* is translated by  $\frac{1}{8}$  to fit the structure into  $P2_1ab$ .) The coordinates of L (unprimed) and D (primed) molecules are related by a nearly perfect non-crystallographic centre of symmetry with respect to the positions marked by an asterisk in Fig. 1. This nearly perfect centre of symmetry is at  $x = \frac{1}{4}, y = \frac{1}{8}, z = \frac{1}{4}$ . The mean deviation of coordinates of the L and D molecules from a perfect centre of symmetry is 0.03 Å. As a consequence of the extra centre of symmetry, the structure also has a nearly perfect non-crystallographic screw about *c*, indicated by positions marked by a cross in Fig. 1.

The bond lengths and angles are given in Table 3. Corresponding bond lengths and angles of the L and D molecules compare well with similar bonds and agree

within the limit of accuracy. The bond lengths and angles agree well with the neutron diffraction study of PA.HCl. The nitro-group distances and angles also agree with literature values.

The carboxyl-group atoms and C<sup>α</sup> of both L and D molecules form a plane, N(1) and N(1') deviating from it by 0.098 and 0.095 Å respectively. The equations of the plane and deviations of atoms from it are given in Table 4 (plane 1). The aromatic ring atoms also form a plane and the deviations of atoms from the mean plane are given in Table 4 (plane 2). As expected, the nitro-group atoms are planar (Table 4, plane 3). The nitro group, however, is not coplanar with the aromatic ring (for both D and L molecules) and there is a twist of about 22.5° about C(7)–N(2). Planes 2 and 3 are inclined at 23.1° for the L and 23.4° for the D molecule.

The conformational angles  $\psi^1$  and  $\psi^2$  of the amino-

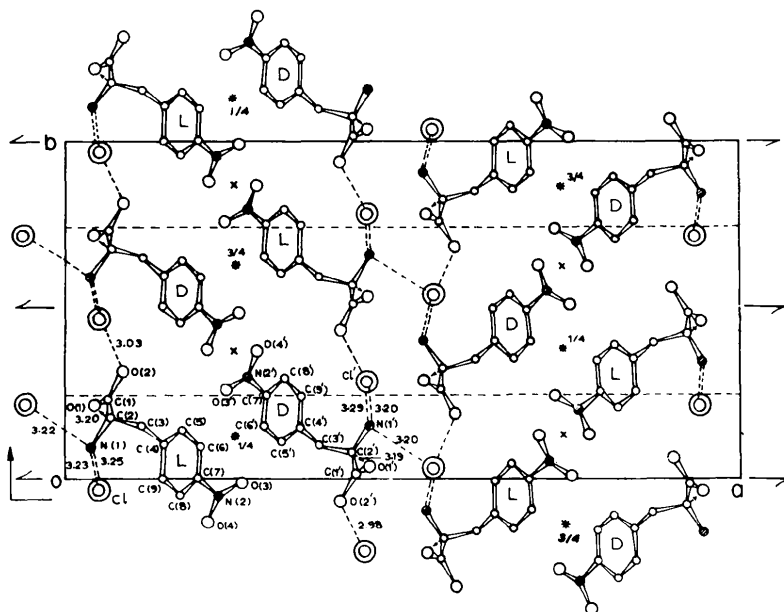
Fig. 1. Projection of the structure down *c*.

Table 3. Bond lengths (Å) and angles (°)

	L Molecule	D Molecule
C(1)–C(2)	1.524 (8)	1.515 (8)
C(2)–C(3)	1.528 (8)	1.535 (8)
C(3)–C(4)	1.513 (8)	1.507 (8)
C(4)–C(5)	1.381 (9)	1.392 (8)
C(5)–C(6)	1.402 (9)	1.385 (9)
C(6)–C(7)	1.374 (8)	1.386 (8)
C(7)–C(8)	1.374 (9)	1.359 (9)
C(8)–C(9)	1.391 (9)	1.400 (9)
C(4)–C(9)	1.399 (8)	1.383 (8)
C(2)–N(1)	1.495 (8)	1.489 (8)
C(7)–N(2)	1.460 (9)	1.472 (8)
C(1)–O(1)	1.190 (7)	1.207 (7)
C(1)–O(2)	1.316 (8)	1.318 (7)
N(2)–O(3)	1.234 (8)	1.214 (8)
N(3)–O(4)	1.211 (8)	1.221 (7)
C(1)–C(2)–C(3)	115.1 (5)	114.2 (4)
C(2)–C(3)–C(4)	114.6 (5)	114.8 (4)
C(3)–C(4)–C(5)	121.8 (5)	121.2 (4)
C(3)–C(4)–C(9)	119.0 (5)	121.2 (4)
C(4)–C(5)–C(6)	121.0 (6)	122.0 (5)
C(5)–C(4)–C(9)	119.2 (5)	117.5 (4)
C(4)–C(9)–C(8)	120.4 (6)	122.1 (5)
C(5)–C(6)–C(7)	117.9 (6)	117.6 (5)
C(6)–C(7)–C(8)	122.8 (6)	123.2 (5)
C(7)–C(8)–C(9)	118.7 (6)	117.5 (5)
C(1)–C(2)–N(1)	107.4 (5)	107.1 (4)
C(3)–C(2)–N(1)	112.4 (5)	112.6 (4)
C(6)–C(7)–N(2)	118.3 (5)	117.0 (4)
C(8)–C(7)–N(2)	118.9 (5)	119.8 (5)
C(2)–C(1)–O(1)	124.3 (5)	124.5 (4)
C(2)–C(1)–O(2)	110.6 (5)	110.8 (4)
O(1)–C(1)–O(2)	125.1 (6)	124.7 (4)
C(7)–N(2)–O(3)	117.9 (6)	118.9 (5)
C(7)–N(2)–O(4)	118.7 (6)	117.4 (5)
O(3)–N(2)–O(4)	123.4 (6)	123.7 (5)

Table 4. Least-squares planes and deviations (Å) of atoms from them

Plane 1: C(1), C(2), O(1) and O(2)			
$0.838x - 0.411y - 0.358z = -0.408$ (L)			
$0.843x - 0.409y - 0.351z = 10.071$ (D)			
	L	D	
C(1)	0.003	-0.005	
C(2)	-0.001	0.001	
O(1)	-0.001	0.002	
O(2)	-0.001	0.002	
N(1)	-0.98	0.095	
Plane 2: C(4), C(5), C(6), C(7), C(8) and C(9)			
$-0.771x + 0.048y - 0.634z = -4.678$ (L)			
$-0.772x + 0.043y - 0.634z = -0.634$ (D)			
	L	D	
C(4)	0.012	-0.012	
C(5)	0.000	-0.001	
C(6)	-0.007	0.013	
C(7)	0.004	-0.011	
C(8)	0.008	-0.003	
C(9)	-0.016	0.015	
N(2)	0.010	-0.019	
O(3)	-0.404	0.403	
O(4)	0.440	-0.448	
Plane 3: C(7), N(2), O(3) and O(4)			
$-0.575x + 0.387y - 0.721z = -3.580$ (L)			
$-0.557x + 0.387y - 0.719z = -5.215$ (D)			
	L	D	
C(7)	0.002	0.000	
N(2)	-0.006	-0.002	
O(3)	0.002	0.001	
O(4)	0.002	0.001	

acid backbone and the angles  $\chi^1$ ,  $\chi^{2,1}$ ,  $\chi^{2,2}$  of the side chain (Lakshminarayanan, Sasisekharan & Ramachandran, 1967) are given in Table 5. There is, in general, good agreement between the conformational parameters of the structure and the observations of Cody, Duax & Hauptman (1973). The  $\chi^1$  parameters of the L and D molecules differ significantly from each other.  $\chi^1$  of the L molecule is also significantly different from  $\chi^1$  of PA.HCl (Al-Karaghoul & Koetzle, 1975). Significant differences are also found between  $\chi^{2,1}$  and  $\chi^{2,2}$  of both L and D molecules and those of PA.HCl.

#### Molecular packing and hydrogen bonding

A view of the packing down *c* is given in Fig. 1 which also indicates the hydrogen bonding. The amino group ( $\text{NH}_3^+$ ) of the L molecule forms three hydrogen bonds with symmetry-related  $\text{Cl}^-$  ions of lengths 3.25, 3.23 and 3.22 Å. The hydroxyl O(2) also forms a hydrogen bond (3.03 Å) with a  $\text{Cl}^-$  ion. The hydrogen bonding is essentially the same as that observed in PA.HCl (Al-Karaghoul & Koetzle, 1975). The amino N(1') of the

D molecule also enters into hydrogen bonds with symmetry-related  $\text{Cl}^-$  ions (3.29, 3.20 and 3.20 Å). Also, the hydroxyl O(2') enters into a hydrogen bond with  $\text{Cl}^-$  (2.98 Å). The hydrogen-bonding scheme is nearly centrosymmetric in nature. Hydrogen-bond lengths and angles are given in Table 6. Apart from the N–H...Cl and O–H...Cl hydrogen bonds, the structure also has C–H...O interactions between the

Table 5. Torsion angles (°)

IUPAC–IUB designation		L	D
$\psi^1$	O(1)–C(1)–C(2)–N(1)	-3.5 (8)	3.1 (8)
$\psi^2$	O(2)–C(1)–C(2)–N(1)	175.9 (5)	-175.9 (5)
$\chi^1$	N(1)–C(2)–C(3)–C(4)	63.6 (6)	-60.9 (6)
$\chi^{2,1}$	C(2)–C(3)–C(4)–C(5)	91.5 (7)	-91.9 (7)
$\chi^{2,2}$	C(2)–C(3)–C(4)–C(9)	-89.6 (7)	89.1 (7)
	C(6)–C(7)–N(2)–O(3)	22.2 (9)	-22.6 (8)
	C(6)–C(7)–N(2)–O(4)	-156.7 (6)	157.7 (6)

Table 6. *Hydrogen-bond distances and angles*

<i>D</i> — <i>H</i> ... <i>A</i>	<i>D</i> ... <i>A</i>	<i>H</i> ... <i>A</i>	∠ <i>H</i> — <i>D</i> ... <i>A</i>
N(1)—H(1)...Cl	3.25 Å	2.38 Å	12°
N(1)—H(2)...Cl <sup>a</sup>	3.23	2.23	10
N(1)—H(3)...Cl <sup>d</sup>	3.22	2.44	21
O(2)—H(4)...Cl <sup>e</sup>	3.03	2.09	23
C(2)—H(5)...O(1) <sup>a</sup>	3.20	2.27	26
N(1')—H(1')...Cl'	3.29	2.45	12
N(1')—H(2')...Cl' <sup>b</sup>	3.20	2.16	9
N(1')—H(3')...Cl' <sup>c</sup>	3.20	2.25	20
O(2')—H(4')...Cl' <sup>f</sup>	2.98	2.06	24
C(2')—H(5')...O(1') <sup>b</sup>	3.19	2.24	25

Symmetry code

(a)	<i>x</i> , <i>y</i> , 1 + <i>z</i>	(d)	$\frac{1}{2} + x - 1$ , $\frac{1}{2} - y$ , <i>z</i>
(b)	<i>x</i> , <i>y</i> , <i>z</i> - 1	(e)	<i>x</i> , $\frac{1}{2} + y$ , - <i>z</i>
(c)	$\frac{1}{2} + x$ , - <i>y</i> , - <i>z</i>	(f)	<i>x</i> , $\frac{1}{2} + y - 1$ , 1 - <i>z</i>

C<sup>α</sup> hydrogen and the carboxyl O(1) translated along **c**, the distances being 3.20 and 3.19 Å for L and D molecules respectively. The hydrogen-bond lengths and angles show that they are clearly C—H...O interactions (Sutor, 1962). In PA.HCl there is a similar interaction (3.26 Å) which has, however, not been termed a

C—H...O bond. In the crystal structure of glycyl-DL-phenylalanine (Marsh, Ramkumar & Venkatesan, 1976) a similar C—H...O interaction is observed.

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### Structure Cristalline de Complexes Moléculaires en Série Naphtoquinonique. III. Structure et Caractéristiques Thermodynamiques du Complexe 2 : 1 entre la Naphtoquinone-1,4 et la Napthohydroquinone-1,4

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The crystal of the 2:1 molecular complex between 1,4-naphthoquinone and 1,4-naphthohydroquinone is triclinic, space group  $P\bar{1}$ , with  $a = 12.745$  (6),  $b = 9.087$  (4),  $c = 11.107$  (4) Å,  $\alpha = 117.10$  (3),  $\beta = 77.16$  (3),  $\gamma = 97.03$  (3)°,  $Z = 2$ . The structure was determined by Patterson and multiresolution methods and refined to  $R = 0.053$  for the 3239 reflexions recorded with a three-circle automatic diffractometer. The structure shows that the molecules are stacked in a planar manner to form an infinite column of triads along the *c* axis. Within a triad the spacings between two consecutive molecules are of the order of 3.40 Å and the overlap is important. Between the triads, there is a gap of 3.50 Å. Each naphthohydroquinone molecule is associated with two naphthoquinone molecules by hydrogen bonding (2.77 Å). By a calorimetric study the heat of formation, the entropy and Gibbs free energy were determined, and the molecular interactions were estimated. Comparison with quinhydrone shows that the naphthoquinone–naphthohydroquinone complex is a weak complex.

#### Introduction

Les naphtoquinones interviennent dans divers processus biologiques, notamment la coagulation sanguine,

où les associations avec le substrat jouent un rôle essentiel.

D'une manière générale, les interactions que peuvent contracter les molécules de naphtoquinone sont mal