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# Neutron Diffraction Study of L-Phenylalanine Hydrochloride*

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A neutron diffraction study of the amino acid salt L-phenylalanine.HCl ($C_9H_{12}NO_2^+Cl^-$) has been carried out. Space group $P2_12_12_1$; $a=27\cdot763$ (17), $b=7\cdot059$ (4), $c=5\cdot380$ (5) Å. The final conventional $R$ value is 0·084 based on 1026 reflections with $F_o^2>\sigma(F_o^2)$, and all bond lengths are determined with a precision better than 0·03 Å. The structure is composed of hydrogen-bonded double layers of phenylalanine molecules joined by N–H···Cl and O–H···Cl hydrogen bonds.

## Introduction

The structure of L-phenylalanine hydrochloride has been solved previously from X-ray diffraction data (Gurskaya & Vainshtein, 1963). A neutron diffraction study of this structure has been carried out in order to determine precise hydrogen atom positions and to elucidate details of hydrogen bonding in this amino acid salt. This work is in connection with a series of neutron diffraction studies of amino acids, peptides, nucleosides, nucleotides and related compounds.

## Crystal data

L-Phenylalanine hydrochloride, $C_6H_5CH_2CH(NH_2)COOH.HCl$; F.W. 201·72. $a=27\cdot763$ (17), $b=7\cdot059$ (4), $c=5\cdot380$ (5) Å. Space group $P2_12_12_1$; $Z=4$. Density $\varrho_{calc}=1\cdot271$, $\varrho_{obs}=1\cdot268$ g cm$^{-3}$ (measured by flotation in a mixture of benzene and carbon tetrachloride). Linear absorption coefficient $\mu=1\cdot898$ cm$^{-1}$.

## Experimental

Crystalline L-phenylalanine hydrochloride was obtained by cooling a boiling saturated solution of L-phenylalanine in 30% hydrochloric acid. The product was recrystallized from water and large single crystals (elongated in the **c** direction) were obtained by slow evaporation of a saturated solution at room temperature. The crystal chosen for this study was approximately 12·8 mm$^3$ in volume, bounded by six major faces and was cleaved at one end with a razor blade. The crystal proved to be hygroscopic and it was enclosed in a sealed quartz tube during neutron data collection. The crystal was mounted with the $c$ axis near the axis of the goniometer head.

Neutron diffraction data were collected at room temperature on an automatic four-circle diffractometer at the Brookhaven High Flux Beam Reactor using the Multiple Spectrometer Control System (Beaucage, Kelly, Ophir, Rankowitz, Spinrad & Van Norton, 1966). Unit-cell parameters were obtained from a least-squares refinement based on the settings of 30 automatically centered reflections well distributed in the reciprocal lattice. Unit-cell parameters obtained in the X-ray study, $a=27\cdot68$ (4), $b=6\cdot98$ (2) and $c=5\cdot34$ (1), are smaller than the neutron parameters and differ from the latter by up to 4$\sigma$ (X-ray).

The intensities of Bragg reflections were measured by the $\theta$–$2\theta$ step-scan technique at a wavelength of 1·2169 (7) Å. The neutron wavelength was determined from observed reflection setting angles for a KBr single crystal ($a=6\cdot600$ Å). The length of the scan was varied according to the formula $\Delta(2\theta)=1\cdot9°\ (1+\tan\theta)$, and the step increment was chosen to give approximately 40 points in each scan. 1599 reflections with $d^*<1\cdot23$ Å$^{-1}$ were measured. Because of the large $a$ axis, it was necessary to use Soller slits in the incident beam to improve the resolution of the diffractometer, and this resulted in decreased beam intensity (about 20% of normal or approximately $1\times10^6$ neutron cm$^{-2}$ sec$^{-1}$). A modified incident-beam collimator was employed during the measurement of 505 reflections with $2\theta>65°$, in order to avoid mechanical collision. This modification changed the beam intensity slightly from that used at lower angles. Background corrections were determined by a method (Lehmann & Larsen, 1974) which divides peak and background in such a way that $\sigma_{count}(I)/I$ is minimized. $I$ is the integrated intensity, and $\sigma(I)$ its standard deviation based on counting statistics. Absorption corrections computed by numerical integration over a Gaussian grid of 400 points were applied to the observed intensities. The linear absorption coefficient was calculated assuming an incoherent scattering cross section for hydrogen of 40 barn and with mass absorption coefficients for C, N, O and Cl taken from *International Tables for X-ray Crystallography* (1962).

Squared observed structure factors were obtained as $F_o^2=I\sin 2\theta$ and were averaged for the two symmetry-related forms $hkl$ and $h\bar{k}l$ to give mean values for 1379 unique reflections. Agreement values are $R_c=$

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$\sum|F_o^2-\bar{F}_o^2|/\sum\bar{F}_o^2=0{\cdot}122$ (low angle) and $R_c=0{\cdot}076$ (high angle), where $\bar{F}_o^2$ is the mean value for symmetry-related reflections.

## Structure refinement

The starting parameters for the refinement were X-ray coordinates for the nonhydrogen atoms given by Gurskaya (1965). Hydrogen atoms were located in a difference-Fourier synthesis and the structure was refined by full-matrix least-squares techniques varying first isotropic and then anisotropic thermal parameters for all 25 atoms and including two scale factors and an isotropic extinction correction parameter $g$ as defined by Zachariasen (1967). Neutron scattering lengths used were: $b_{\rm C}=0{\cdot}6626$, $b_{\rm H}=-0{\cdot}3723$, $b_{\rm N}=0{\cdot}92$, $b_{\rm O}=0{\cdot}575$ and $b_{\rm Cl}=0{\cdot}9584$ ($\times 10^{-12}$ cm) (Shull, 1971; Kvick, Koetzle, Thomas & Takusagawa, 1974). The function minimized in the refinements was $\sum w|F_o^2-|F_c|^2|^2$, where $w=1/\sigma^2$ and $\sigma^2=\sigma^2_{\rm count}+(0{\cdot}02F_o^2)^2$. In order to avoid biasing the results, weak reflections with $F_o^2<0$ were included in the refinements (Hirshfeld & Rabinovich, 1973). Very little extinction was found; the majority of reflections have extinction corrections (on $F^2$) near unity. Very few reflections have $E^2=0{\cdot}8$–$0{\cdot}9$ and the strongest reflection (800) has $E^2=0{\cdot}68$. In the last cycle, no parameter shifted by more than $0{\cdot}3\sigma$. No systematic dependence of values of $w|F_o^2-|F_c|^2|^2$ on $F_o^2$ was observed, as one would expect for a proper weighting scheme. Agreement values are $R=\sum|F_o^2-|F_c|^2|/\sum|F_o^2|=0{\cdot}130$ and $R_w=[\sum w|F_o^2-|F_c|^2|^2/\sum wF_o^4]^{1/2}=0{\cdot}112$. These high $R$ values are mainly due to the large number of weak reflections in the data set.

Removal of reflections with $F_o^2<\sigma$ (353 reflections) decreased $R$ and $R_w$ to 0·104 and 0·99 respectively, and in this case the value of the conventional agreement value given by $\sum|F_o-|F_c||/\sum F_o$ is 0·084. The standard error of fit with all data included is $S=\{\sum w|F_o^2-|F_c|^2|^2/(n_o-n_v)\}^{1/2}=1{\cdot}35$, where $n_o$ and $n_v$ are the number of observed reflections and number of variables respectively.

The refined atomic parameters are given in Table 1 and final values for the observed and calculated squared structure factors are listed in Table 2.* The final value of the extinction coefficient $g$ is 0·41 (6) $\times 10^4$.

## Discussion

A stereoscopic view of the protonated phenylalanine molecule is shown in Fig. 1. Covalent bond lengths and angles are given in Tables 3 and 4, respectively which include for comparison results from the prior X-ray study (Gurskaya, 1965). The general features of the nonhydrogen backbone in the present neutron study and in the X-ray study are the same, and bond distances agree to within $3\sigma$ (X-ray). However, the X-ray standard deviations are three to four times larger than the neutron values and the X-ray coordinates of $C^{\varepsilon2}$ and $C^{\zeta}$ were idealized. A maximum discrepancy of 0·079 Å was observed in the length of the bond $C^{\beta}$–$C^{\gamma}$; here the X-ray value of 1·578 Å is

Table 1. *Fractional coordinates and temperature parameters*

The form of the anisotropic Debye–Waller factor is $\exp\{-2\pi^2[U_{11}(ha^*)^2+U_{22}(kb^*)^2+U_{33}(lc^*)^2+2U_{12}ha^*kb^*+2U_{13}ha^*lc^*+2U_{23}kb^*lc^*]\}$. The $U_{ij}$'s are multiplied by $10^4$.

| | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cl | 0·0565 (1) | 0·1508 (5) | 0·9737 (7) | 17 (1) | 177 (8) | 288 (15) | −5 (2) | −1 (3) | 86 (12) |
| $O^1$ | 0·0455 (2) | 0·6606 (9) | 0·1320 (11) | 18 (1) | 199 (15) | 208 (23) | −6 (4) | −15 (5) | 53 (18) |
| $O^2$ | 0·0861 (3) | 0·8697 (9) | 0·3608 (15) | 26 (2) | 156 (17) | 428 (36) | −11 (4) | −49 (6) | 40 (23) |
| C | 0·0654 (2) | 0·7049 (7) | 0·3205 (9) | 14 (1) | 142 (12) | 176 (20) | 0 (3) | −6 (4) | 32 (14) |
| $C^{\alpha}$ | 0·0693 (2) | 0·5785 (7) | 0·5487 (9) | 13 (1) | 156 (11) | 123 (17) | 3 (3) | 0 (3) | 17 (14) |
| $C^{\beta}$ | 0·1206 (2) | 0·5437 (9) | 0·6352 (11) | 13 (1) | 224 (16) | 174 (21) | −3 (3) | −7 (4) | 33 (17) |
| N | 0·0421 (2) | 0·4022 (6) | 0·4934 (8) | 13 (1) | 175 (9) | 189 (17) | −1 (2) | −7 (3) | 53 (13) |
| $C^{\gamma}$ | 0·1527 (2) | 0·4424 (8) | 0·4549 (11) | 10 (1) | 206 (13) | 266 (22) | −1 (3) | −7 (4) | 23 (17) |
| $C^{\delta1}$ | 0·1765 (2) | 0·5440 (12) | 0·2688 (13) | 12 (1) | 383 (23) | 275 (28) | −2 (4) | −1 (5) | 47 (26) |
| $C^{\delta2}$ | 0·1597 (3) | 0·2474 (10) | 0·4732 (21) | 17 (1) | 208 (19) | 771 (55) | 12 (4) | −7 (7) | −25 (27) |
| $C^{\varepsilon1}$ | 0·2063 (3) | 0·4533 (19) | 0·1001 (17) | 14 (1) | 606 (36) | 489 (44) | 17 (6) | 12 (6) | −28 (35) |
| $C^{\varepsilon2}$ | 0·1898 (3) | 0·1528 (14) | 0·3055 (24) | 19 (2) | 279 (22) | 1160 (75) | 9 (5) | 15 (9) | −176 (39) |
| $C^{\zeta}$ | 0·2126 (3) | 0·2573 (19) | 0·1165 (22) | 16 (2) | 647 (45) | 692 (60) | 14 (7) | −8 (8) | −300 (43) |
| $H^1$ | 0·0527 (4) | 0·3394 (17) | 0·3223 (22) | 21 (2) | 262 (28) | 234 (41) | −3 (7) | 15 (8) | −26 (34) |
| $H^2$ | 0·0466 (4) | 0·3064 (17) | 0·6357 (20) | 22 (2) | 249 (27) | 210 (38) | −7 (7) | 2 (8) | 177 (32) |
| $H^3$ | 0·0072 (4) | 0·4322 (17) | 0·4794 (23) | 17 (2) | 320 (28) | 375 (49) | −7 (7) | −12 (10) | −28 (46) |
| $H^{02}$ | 0·0809 (5) | 0·9587 (14) | 0·2173 (24) | 29 (3) | 184 (25) | 377 (54) | −6 (7) | −32 (10) | 142 (35) |
| $H^{\alpha}$ | 0·0498 (4) | 0·6507 (17) | 0·7003 (21) | 22 (2) | 255 (28) | 226 (41) | 0 (7) | 10 (8) | 13 (33) |
| $H^{\beta1}$ | 0·1357 (5) | 0·6795 (18) | 0·6850 (25) | 21 (2) | 280 (30) | 409 (56) | −24 (7) | −21 (10) | −77 (42) |
| $H^{\beta2}$ | 0·1183 (4) | 0·4639 (17) | 0·8097 (21) | 19 (2) | 366 (34) | 302 (47) | 7 (7) | 6 (8) | 173 (40) |
| $H^{\delta1}$ | 0·1710 (5) | 0·6884 (26) | 0·2583 (31) | 27·(3) | 386 (41) | 580 (79) | −9 (10) | 25 (12) | 235 (57) |
| $H^{\delta2}$ | 0·1422 (6) | 0·1718 (21) | 0·6190 (39) | 22 (3) | 301 (41) | 1141 (134) | 17 (9) | 15 (16) | 170 (61) |
| $H^{\varepsilon1}$ | 0·2234 (6) | 0·5300 (38) | −0·0411 (33) | 25 (3) | 1129 (117) | 488 (76) | 23 (15) | 40 (14) | 195 (93) |
| $H^{\varepsilon2}$ | 0·1947 (7) | 0·0103 (27) | 0·3112 (56) | 39 (5) | 371 (48) | 2012 (218) | 31 (12) | 56 (26) | −409 (96) |
| $H^{\zeta}$ | 0·2348 (7) | 0·1879 (36) | −0·0138 (49) | 24 (3) | 961 (102) | 1338 (172) | −1 (15) | 34 (20) | −677 (129) |

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* Table 2 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31053 (9pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

clearly too high while the neutron value of 1·499 (8) Å (1·511 Å corrected for thermal motion) is almost the same as that found in L-tyrosine and L-tyrosine.HCl (Frey, Koetzle, Lehmann & Hamilton, 1973).

The bond $C-O^1$ is shorter than $C-O^2$ by 0·124 Å (corrected); $C-O^1$ is a double bond and the extra proton which neutralizes the carboxyl group is bonded to $O^2$. $C^{\alpha}$ and the carboxyl group ($O^1$,$O^2$,C) are coplanar; the maximum deviation from the least-squares plane through these four atoms is 0·005 Å. The nitrogen atom lies 0·089 Å from this plane. The torsion angles (Table 5) $\chi^1$ and $\chi^2$ are $-2{\cdot}9$ and 176·1°, respectively.

Atom $C^{\beta}$ is coplanar with the benzene ring and the maximum deviation from the plane is 0·006 Å in this group. Also the torsion angle difference $\chi^{2,1}-\chi^{2,2}=180{\cdot}9$ (Table 5) which clearly indicates that the group $C^{\beta}-C^{\gamma}-C^{\delta 1}-C^{\delta 2}$ is planar (Cody, Duax & Hauptman, 1973).

Hydrogen atom positions given in the X-ray study (Gurskaya, 1965) have been calculated according to the positions of the 'heavy' atoms or located on an

Table 3. *Distances* (Å) *within the molecule*

| Bonds | Neutron | Corrected for thermal motion | X-ray* |
|---|---|---|---|
| $C-O^1$ | 1·196 (8) | 1·205 | 1·173 |
| $C-O^2$ | 1·316 (8) | 1·329 | 1·357 |
| $O^2-H^{02}$ | 1·006 (16) | 1·007 | |
| $C-C^{\alpha}$ | 1·522 (7) | 1·532 | 1·510 |
| $C^{\alpha}-H^{\alpha}$ | 1·103 (15) | 1·107 | |
| $C^{\alpha}-N$ | 1·485 (6) | 1·499 | 1·489 |
| $N-H^1$ | 1·063 (14) | 1·067 | |
| $N-H^2$ | 1·029 (13) | 1·034 | |
| $N-H^3$ | 0·996 (15) | 1·001 | |
| $C^{\alpha}-C^{\beta}$ | 1·519 (7) | 1·530 | 1·555 |
| $C^{\beta}-C^{\gamma}$ | 1·499 (8) | 1·511 | 1·578 |
| $C^{\beta}-H^{\beta 1}$ | 1·080 (15) | 1·087 | |
| $C^{\beta}-H^{\beta 2}$ | 1·097 (14) | 1·102 | |
| $C^{\gamma}-C^{\delta 1}$ | 1·397 (9) | 1·416 | 1·372 |
| $C^{\delta 1}-H^{\delta 1}$ | 1·032 (25) | 1·041 | |
| $C^{\gamma}-C^{\delta 2}$ | 1·394 (9) | 1·416 | 1·374 |
| $C^{\delta 2}-H^{\delta 2}$ | 1·066 (24) | 1·072 | |
| $C^{\delta 1}-C^{\varepsilon 1}$ | 1·387 (11) | 1·397 | 1·393 |
| $C^{\varepsilon 1}-H^{\varepsilon 1}$ | 1·047 (26) | 1·061 | |
| $C^{\delta 2}-C^{\varepsilon 2}$ | 1·399 (12) | 1·410 | 1·390 |
| $C^{\varepsilon 2}-H^{\varepsilon 2}$ | 1·016 (26) | 1·030 | |
| $C^{\varepsilon 1}-C^{\zeta}$ | 1·397 (14) | 1·419 | 1·392 |
| $C^{\varepsilon 2}-C^{\zeta}$ | 1·406 (14) | 1·426 | 1·441 |
| $C^{\zeta}-H^{\zeta}$ | 1·054 (29) | 1·067 | |

* Recalculated using our unit-cell dimensions. $\sigma=0{\cdot}02$–0·03 Å.

Table 4. *Angles* (°) *within the molecule*

| | Neutron | X-ray* |
|---|---|---|
| $C-O^2-H^{02}$ | 111·2 (9) | |
| $O^1-C-O^2$ | 125·0 (6) | 123·8 |
| $O^1-C-C^{\alpha}$ | 124·3 (5) | 127·0 |
| $O^2-C-C^{\alpha}$ | 110·7 (5) | 109·2 |
| $C-C^{\alpha}-H^{\alpha}$ | 106·9 (7) | |
| $C-C^{\alpha}-N$ | 107·1 (4) | 105·8 |
| $C-C^{\alpha}-C^{\beta}$ | 114·1 (4) | 115·9 |
| $H^{\alpha}-C^{\alpha}-N$ | 106·7 (7) | |
| $H^{\alpha}-C^{\alpha}-C^{\beta}$ | 107·9 (7) | |
| $N-C^{\alpha}-C^{\beta}$ | 113·7 (4) | 112·2 |
| $C^{\alpha}-N-H^1$ | 112·5 (7) | |
| $C^{\alpha}-N-H^2$ | 109·9 (7) | |
| $C^{\alpha}-N-H^3$ | 109·3 (7) | |
| $H^1-N-H^2$ | 109·7 (9) | |
| $H^1-N-H^3$ | 107·0 (9) | |
| $H^2-N-H^3$ | 108·3 (10) | |
| $C^{\alpha}-C^{\beta}-C^{\gamma}$ | 115·9 (5) | 113·2 |
| $C^{\alpha}-C^{\beta}-H^{\beta 1}$ | 107·2 (8) | |
| $C^{\alpha}-C^{\beta}-H^{\beta 2}$ | 106·9 (7) | |
| $H^{\beta 2}-C^{\beta}-C^{\gamma}$ | 110·1 (7) | |
| $H^{\beta 2}-C^{\beta}-H^{\beta 1}$ | 105·4 (10) | |
| $C^{\gamma}-C^{\beta}-H^{\beta 1}$ | 110·7 (8) | |
| $C^{\beta}-C^{\gamma}-C^{\delta 1}$ | 120·0 (6) | 120·3 |
| $C^{\beta}-C^{\gamma}-C^{\delta 2}$ | 120·5 (7) | 118·1 |
| $C^{\delta 1}-C^{\gamma}-C^{\delta 2}$ | 119·5 (8) | |
| $C^{\gamma}-C^{\delta 1}-H^{\delta 1}$ | 118·4 (9) | |
| $C^{\gamma}-C^{\delta 1}-C^{\varepsilon 1}$ | 120·9 (9) | 122·1 |
| $H^{\delta 1}-C^{\delta 1}-C^{\varepsilon 1}$ | 120·6 (11) | |
| $C^{\gamma}-C^{\delta 2}-C^{\varepsilon 2}$ | 120·6 (10) | 118·4 |
| $C^{\gamma}-C^{\delta 2}-H^{\delta 2}$ | 118·9 (11) | |
| $C^{\varepsilon 2}-C^{\delta 2}-H^{\delta 2}$ | 120·6 (10) | |
| $C^{\delta 1}-C^{\varepsilon 1}-H^{\varepsilon 1}$ | 120·5 (15) | |
| $C^{\delta 1}-C^{\varepsilon 1}-C^{\zeta}$ | 119·4 (11) | 117·9 |
| $H^{\varepsilon 1}-C^{\varepsilon 1}-C^{\zeta}$ | 120·1 (15) | |
| $C^{\delta 2}-C^{\varepsilon 2}-C^{\zeta}$ | 119·0 (10) | 120·5 |
| $C^{\delta 2}-C^{\varepsilon 2}-H^{\varepsilon 2}$ | 122·2 (17) | |
| $C^{\zeta}-C^{\varepsilon 2}-H^{\varepsilon 2}$ | 118·8 (16) | |
| $C^{\varepsilon 1}-C^{\zeta}-H^{\zeta}$ | 119·4 (18) | |
| $C^{\varepsilon 1}-C^{\zeta}-C^{\varepsilon 2}$ | 120·6 (11) | 119·5 |
| $H^{\zeta}-C^{\zeta}-C^{\varepsilon 2}$ | 120·0 (17) | |

* Recalculated using our unit-cell dimensions.

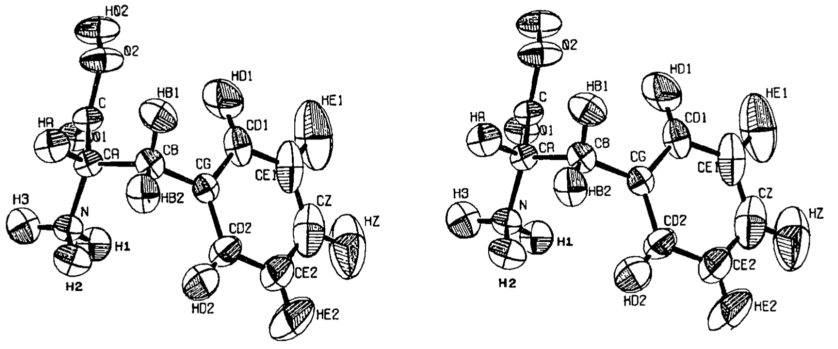

Fig. 1. Stereoscopic drawing of L-phenylalanine cation with thermal ellipsoids drawn on a 40% probability scale. The letters *A*, *B*, *G*, *D*, *E* and *Z* correspond to the designations α, β, γ, δ, ε, and ζ.

Table 5. *Torsion angles* (°)

| IUPAC-IUB designation | Atoms involved | Angle |
|---|---|---|
| $\Phi^1$ | C—C$^\alpha$–N–H$^1$ | 51·7 (9) |
| $\Phi^2$ | C—C$^\alpha$–N–H$^2$ | 174·3 (8) |
| $\Phi^3$ | C—C$^\alpha$–N–H$^3$ | −67·0 (9) |
| $\psi^1$ | O$^1$–C—C$^\alpha$–N | −2·9 (8) |
| $\psi^2$ | O$^2$–C—C$^\alpha$–N | 176·1 (5) |
| $\chi^1$ | N—C$^\alpha$–C$^\beta$–C$^\gamma$ | 60·7 (6) |
| $\chi^{2,1}$ | C$^\alpha$–C$^\beta$–C$^\gamma$–C$^{\delta 1}$ | 84·2 (7) |
| $\chi^{2,2}$ | C$^\alpha$–C$^\beta$–C$^\gamma$–C$^{\delta 2}$ | −96·7 (7) |

electron density map but they have not been refined. Thus it is not appropriate to make a comparison of results involving hydrogen atoms between the present neutron study and the X-ray study. Besides, the $z$ coordinates for some of the hydrogen atoms in the X-ray study seem to have been miscalculated.

The molecular packing in one unit cell of the structure is shown in Fig. 2. There are layers of phenylalanine molecules connected by chloride ions *via* a system of hydrogen bonds. Each chloride ion joins three molecules of one layer *via* H$^1$, H$^2$ and H$^{02}$ and connects these *via* H$^3$ to a fourth molecule in a second layer, thus forming a system of double layers. These double layers are parallel to the 100 plane. The only interaction forces between the double layers are the weak van der Waals forces, which explains the observation that the crystals cleave easily along the 100 face. This kind of molecular arrangement is characteristic for structures containing both polar and non-polar groups together. L-Tryptophane hydrochloride (Takigawa, Ashida, Sasada & Kakudo, 1966; Andrews, Farkas, Frey, Lehmann & Koetzle, 1974) and glycine hydrochloride (Al-Karaghouli, Cole, Lehmann, Miskell, Verbist & Koetzle, 1975) afford additional examples of this type of packing. Hydrogen-bond distances and angles in L-phenylalanine hydrochloride are given in Table 6. The intermolecular distance between H$^3$ and the carboxyl oxygen O$^1$ within the double layer is 2·484 (15) Å (the corresponding O$^1\cdots$N distance being 3·046 (8) Å) which is somewhat more than the sum of van der Waals radii of 2·40 Å for hydrogen and oxygen. Here, we have taken the hydrogen radius to be 1·0 Å as recommended by Baur (1972). Thus H$^3$ cannot be envisaged to form a 'bifurcated' hydrogen bond as suggested by Gurskaya (1965) on the basis of the X-ray O–N distances.

Table 6. *Distances* (Å) *and angles* (°) *in the hydrogen bonds*

| A–H$\cdots$Cl | A$\cdots$Cl | H$\cdots$Cl | ∠A–H$\cdots$Cl |
|---|---|---|---|
| N–H$^1\cdots$Cl | 3·336 (7) | 2·303 (13) | 163·6 (9) |
| N–H$^2\cdots$Cl | 3·160 (6) | 2·142 (12) | 169·8 (10) |
| N–H$^3\cdots$Cl | 3·257 (6) | 2·360 (14) | 149·4 (9) |
| O$^2$–H$^{02}\cdots$Cl | 2·992 (8) | 2·004 (12) | 166·8 (11) |

Bond lengths have been corrected for the foreshortening effects of thermal motion. Corrections to bond angles are very small and these have been neglected. The thermal parameters of the nonhydrogen atom backbone were fitted to rigid body motions by the method of Schomaker & Trueblood (1968) assuming the molecule is composed of two rigid groups (O$^1$, O$^2$, C, C$^\alpha$, C$^\beta$ and C$^\beta$ plus the benzene ring). The r.m.s. difference between observed and calculated thermal parameters $U_{ij}$ for the two rigid bodies is 0·003 and 0·005 Å$^2$, respectively. The calculated rigid-body librations were used to derive corrections to the

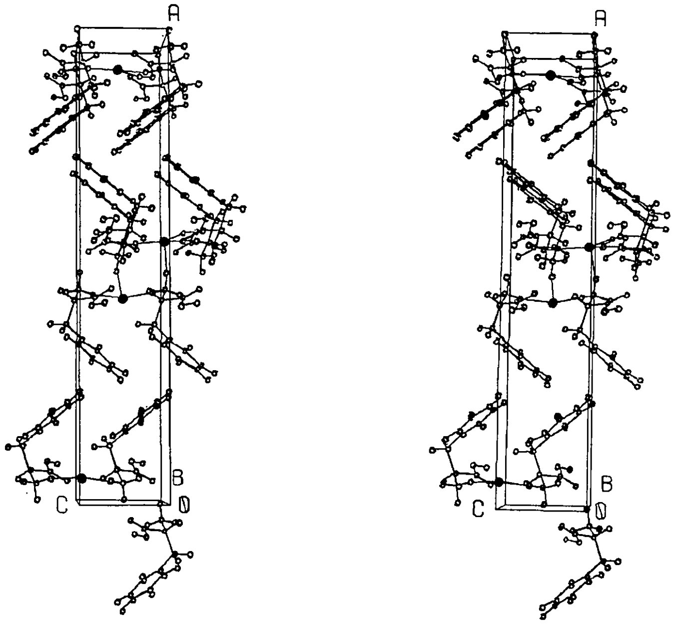

Fig. 2. Stereoscopic view of the packing within one unit cell. Chloride ions have been shaded.

C–C, C–N and C–O bond distances. Bond distances involving hydrogen atoms were corrected for the effects of thermal motion using the minimum correction of Busing & Levy (1964). Average bond lengths in the benzene ring are: C–C = 1·397 Å (uncorrected) and 1·414 Å (corrected); C–H = 1·043 Å (uncorrected) and 1·054 Å (corrected). These values may be compared with the spectroscopic values from benzene of $r_0$(C–C) = 1·397 (1) Å and $r_0$(C–H) = 1·084 (5) Å (Langseth & Stoicheff, 1956). Obviously, the corrections to our C–H distances have been underestimated somewhat; with the rigid-body model we obtain a mean corrected C–H distance in the ring of 1·057 Å. The exact agreement between our uncorrected mean benzene C–C distance and the spectroscopic value is probably fortuitous. Average corrected C–H bond lengths in the side chain are 1·099 Å (minimum correction) and 1·104 Å (rigid-body correction).

In order to obtain an estimate of the barrier height for torsional motion of the ammonium group, an additional rigid-body calculation was carried out (assuming atoms $H^1$, $H^2$, $H^3$, N and $C^\alpha$ behave as a rigid body) yielding an r.m.s. difference between observed and calculated $U_{ij}$ of 0·004 $Å^2$. The largest principal axis of the libration tensor **L** lies approximately 35° from the ammonium group's threefold axis and has an r.m.s. librational amplitude of 11 (1)°. With the assumption of a harmonic oscillator approximation to a threefold cosine hindered rotor (Schlemper, Hamilton & La Placa, 1971), this librational amplitude corresponds to $\nu = 276$ cm$^{-1}$ and potential barrier $V_0 = 4{\cdot}1$ kcal mole$^{-1}$. This barrier is somewhat less than the average value of 4·8 kcal mole$^{-1}$ obtained for ammonium groups in four other amino acid hydrochlorides (Jones, Bernal, Frey & Koetzle, 1974). The difference may be due to the double-layered nature of the hydrogen-bonding system in L-phenylalanine hydrochloride as compared to the rather stronger three-dimensional network of hydrogen bonding in the other hydrochlorides. The thermal parameters in the benzene ring are generally higher than those in the rest of the molecule. This may be explained by the relative freedom of motion of the rings, which are held in the crystal by van der Waals and stacking forces, compared to the carboxyl and ammonium groups, which are bound together with chloride ions in a system of hydrogen bonds as described above. Similarly, high isotropic thermal parameters have been found for the ring carbon atoms in the X-ray study (Gurskaya, 1965).

Bond distances and angles determined in this study have standard deviations approximately two to four times larger than those found in the most precise neutron diffraction structure refinements. The reason for these high $\sigma$ values is the large number of very weak reflections. Slightly more than one-quarter of the observed reflections had intensities below $\sigma$; there were only 4·5 reflections above $\sigma$ for each refined parameter. We have attempted to avoid bias in our results by refining on $F^2$ and by including all weak reflections; our final analysis of variance shows no evidence of systematic errors.

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