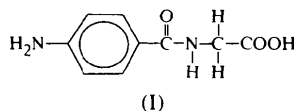


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[*Z. Kristallogr.* (1993), **207**, 53–58] and with the structure of the parent molecule, hippuric acid.

Comment

This study of 4-aminohippuric acid, (I), is one of a series on hydrogen bonding in amino-substituted cyclic carboxylic acids which includes 4-aminoquinoline-2-carboxylic acid monohydrate (Burd *et al.*, 1997), and 3-aminopyrazine-2-carboxylic acid, 2-aminonicotinic acid and 3-aminopyrazole-4-carboxylic acid (Dobson & Gerkin, 1996, 1997, 1998). Although a structure of (I) has been reported by Chakrabarti & Dattagupta (1993) (hereafter, CD), the H atoms were not refined and the s.u.'s of most metrical parameters appeared large, although no specific experimental difficulties were cited. The present interest is, *via* a structure redetermination, to determine and describe the hydrogen bonding more precisely and more fully than did the previous study.



The title acid crystallized in the non-centrosymmetric space group $P2_12_12_1$ with one molecule in the asymmetric unit, in agreement with CD; the cell edges are in moderate agreement with CD, the greatest difference being 0.06 Å in the *b* edge (present indexing). The refined molecule and the numbering scheme are shown in Fig. 1. In this molecule, there are three potential hydrogen-bond donors (O1, N1 and N2) with four potential hydrogen-bonding H atoms (H1, H1N1, H1N2 and H2N2), and five potential hydrogen-bond acceptors (O1, O2, O3, N1 and N2). Four hydrogen bonds in fact occur (in agreement with CD); these involve all the potential donors and their H atoms, but only the three O atoms of the five potential acceptors just cited. The H atoms in these bonds are ordered, and proton transfer from the carboxyl group to the amino group does not occur in this structure. Hydrogen-bond geometrical parameters are given in Table 2. Overall, the angular geometries in particular are not in good agreement with those reported by CD: in the order given in Table 2, these angles are 164 (2) *versus* 142, 173 (2) *versus* 170, 163 (2) *versus* 130, and 167 (2) *versus* 154°, respectively; moreover, in each case, the angle found in the present study is larger. The results of hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995) for the first- and basic second-level graphs for these four bonds (labelled *a–d*, for this purpose, in the same order as Table 2) are given in Table 3. Cyclic hydrogen-bonded dimers are not formed; through second-level graphs, only chain patterns occur. In the order of their occurrence in Table 3, these chains propagate along **a**, **b**, **a**, **b**, **c**, **c**, **b**, **a** and **a**, and gen-

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Hydrogen bonding in 4-aminohippuric acid

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Abstract

The title acid, C₉H₁₀N₂O₃, crystallized in the non-centrosymmetric space group $P2_12_12_1$ with one molecule in the asymmetric unit. Four hydrogen bonds occur whose donor–acceptor distances are: O1···O3 2.630 (2), N1···O3 3.090 (2), N2···O1 3.099 (2), and N2···O2 3.022 (2) Å, and whose angles fall in the range 163 (2)–173 (2)°. The H atoms in these bonds are ordered. Cyclic hydrogen-bonded dimers are not formed; through second-level graphs, only hydrogen-bonded chains occur. These form a strongly three-dimensional array of hydrogen bonds. The dihedral angle between the core plane and the carboxyl plane is 54.8 (2)°, and between the core plane and the plane of the amino group, 34 (1)°. The structure is compared with a previous determination by Chakrabarti & Dattagupta

erate a strongly three-dimensionally hydrogen-bonded structure. These bonds link a given molecule to eight neighboring molecules, as shown in Fig. 2. The basic third- and fourth(highest)-level graphs are also all chains whose descriptors and directions of propagation are: for bonds *abc*: $C_3^2(12)$, **b**; for *abd*: $C_3^2(14)$, **c**; for *acd*: $C_3^2(11)$, **a**; for *bcd*: $C_3^2(14)$, **b**; and, for *abcd*: $C_3^2(11)$, **c**. Edge-sharing rings arise as complex graphs at the third level. Examples include: for bonds *abc*, $R_3^3(18)$; for *abd*, $R_6^4(28)$; and, for *acd*, $R_3^3(13)$ and the somewhat larger $R_3^3(21)$. The strongest intermolecular C—H···O interaction, C2—H2···O3ⁱⁱ [symmetry code: (ii) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$], has C···O = 3.299 (2), H···O = 2.45 (2) Å

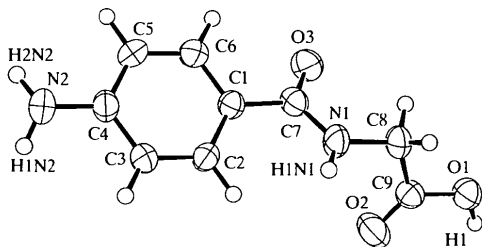


Fig. 1. ORTEPII (Johnson, 1976) drawing of (I), showing our numbering scheme. Displacement ellipsoids are drawn for 50% probability for all atoms except H, for which they have been set artificially small.

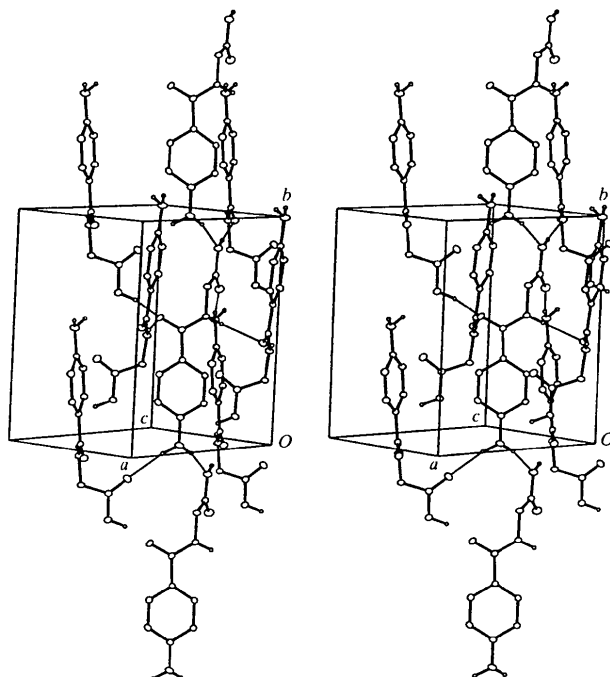


Fig. 2. ORTEPII (Johnson, 1976) drawing of a central 4-aminohippuric acid molecule and the eight neighboring molecules linked to it by hydrogen bonds (which are depicted by the finer lines). Displacement ellipsoids have been set artificially small, and H atoms not involved in hydrogen bonding have been omitted for clarity.

and C—H···O = 143 (1)°; the same two molecules are also, however, hydrogen bonded *via* N1—H1N1···O3ⁱⁱ.

The benzene core is very nearly planar; the maximum deviation of an atom from the best-fit plane describing the ring is 0.004 (2) Å, while the average deviation is 0.002 (2) Å. The dihedral angle between the core plane and the plane of the carboxyl group is 54.8 (2)°, and that between the core plane and the amino group plane (N2, H1N2, H2N2) is 34 (1)°. Atoms C7, O3, N1 and C8 of the amide chain at C1 also lie essentially in a plane, the maximum deviation of an atom from the best-fit plane through them being 0.002 (2) Å; the carboxyl-C atom, C9, lies 1.329 (2) Å out of this plane. The dihedral angle between the amide plane and the core plane is 20.9 (1)°, and between the amide plane and the carboxyl group plane, 75.7 (2)°; these values are similar to the corresponding values for hippuric acid: 13.9 and 87.8° (Harrison *et al.*, 1972).

Intramolecular distances and angles of (I) which are of particular interest are given in Table 1. All distances and angles fall within normal limits. The geometry of the non-H atoms of the amide chain at C1 can be compared with that of the corresponding chain in the parent hippuric acid as determined by Ringertz (1971), Harrison *et al.* (1972) and Currie & Macdonald (1974), as well as with the previous results of CD for (I). Distances and angles in the chain for hippuric acid are taken as the mean of the values given for the three studies cited; the resulting s.u.'s of the mean values are 0.004 Å for distances and 0.2° for angles. The average deviation between the resulting seven average distances for the hippuric acid amide chain and the corresponding distances found here for (I) is 0.007 Å; correspondingly, the average deviation for the ten angles is 0.5°. (The s.u.'s for the present study are 0.002 Å for distances and 0.2° for angles.) These results strongly support, in detail, the geometry of the amide chain of (I) as reported in this study. The (absolute) agreement is not as good with the results from CD (whose s.u.'s for distances average 0.009 Å, and for angles, 0.6°); thus, the average deviation between seven corresponding distances as given in CD and in this study for the amide chain at C1 is 0.015 Å, and for ten corresponding angles, 1.6°. Moreover, the greatest deviation in corresponding distances, 0.039 Å, occurs for C9—O1, which may be reflected in some of the differences in hydrogen-bonding geometry detailed above. With respect to chemically equivalent bonds of the benzene ring (C1—C6 = C1—C2, C2—C3 = C5—C6, and C3—C4 = C4—C5), the present results for (I) are in closer (absolute) agreement with the mean results for hippuric acid than with the results of CD for (I): the mean difference between corresponding members of these three pairs of distances is 0.003 Å for this study, 0.006 Å for the mean hippuric acid and 0.013 Å for CD. On the other hand, agreement is fortuitously good between the present values and the corresponding CD values of six torsion angles tabulated

in CD: the average deviation between them is 0.6°, only approximately half the mean s.u. of the CD values for these angles.

In summary, the higher precision realised in the present study and the successful refinement of H atoms yield parameter values which supersede those of CD. Determination of the absolute structure, however, was not possible.

The closest intermolecular approaches found here for (D), excluding pairs of atoms in groups directly involved in hydrogen bonding or in the C—H...O interaction described above, are between C7 and H1N1^v [symmetry code: (v) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$], and fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.24 Å. It may be noted that these pairs of atoms are in molecules hydrogen bonded to each other.

Experimental

4-Aminohippuric acid of stated purity 97% was obtained from the Aldrich Chemical Company. As received, it was dissolved in ethanol, and the solution was filtered. Slow evaporation at room temperature produced satisfactory crystals.

Crystal data

C₉H₁₀N₂O₃
M_r = 194.19
 Orthorhombic
*P*2₁2₁2₁
a = 10.253 (1) Å
b = 11.2035 (9) Å
c = 8.008 (1) Å
V = 919.9 (2) Å³
Z = 4
D_x = 1.402 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 15.1–17.5°
 μ = 0.107 mm⁻¹
T = 296 K
 Slant prism
 0.38 × 0.36 × 0.29 mm
 Pale amber

Data collection

AFC-5S diffractometer
 ω scans
 Absorption correction: none
 2355 measured reflections
 2125 independent reflections
 1715 reflections with
 $I > 2\sigma_I$
R_{int} = 0.022

θ_{\max} = 27.56°
 h = 0 → 13
 k = 0 → 14
 l = -10 → 10
 6 standard reflections
 every 150 reflections
 intensity decay: 3.85%

Refinement

Refinement on *F*²
R(*F*) = 0.036
 $wR(F^2)$ = 0.059
S = 1.76
 2124 reflections
 168 parameters
 All H atoms refined
 $w = 1/\sigma^2(F^2)$
 $(\Delta/\sigma)_{\max} < 0.01$

$\Delta\rho_{\max}$ = 0.22 e Å⁻³
 $\Delta\rho_{\min}$ = -0.17 e Å⁻³
 Extinction correction:
 Zachariasen (1963, 1968)
 Extinction coefficient:
 $4.2(2) \times 10^{-6}$
 Scattering factors from
 Stewart *et al.* (1965) (H)
 and Creagh & McAuley
 (1992) (C, N, O)

Table 1. Selected geometric parameters (Å, °)

O1—C9	1.327 (2)	N1—C7	1.337 (2)
O2—C9	1.195 (2)	N1—C8	1.454 (2)
O3—C7	1.244 (2)	N2—C4	1.373 (2)
O1—C9—O2	124.6 (2)	O2—C9—C8	125.9 (2)
O1—C9—C8	109.6 (2)		

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...O3 ⁱ	0.95 (2)	1.70 (2)	2.630 (2)	164 (2)
N1—H1N1...O3 ⁱⁱ	0.89 (2)	2.23 (2)	3.090 (2)	173 (2)
N2—H1N2...O1 ⁱⁱⁱ	0.91 (2)	2.22 (2)	3.099 (2)	163 (2)
N2—H2N2...O2 ^{iv}	0.93 (2)	2.10 (2)	3.022 (2)	167 (2)

Symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$; (ii) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (iii) $x, y - 1, z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$.

Table 3. First- and basic second-level graph-set descriptors involving hydrogen bonds which are designated *a–d* in the order given in Table 2

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
<i>a</i>	<i>C</i> (7)	<i>C</i> ₂ ¹ (7)	<i>C</i> ₃ ² (10)	<i>C</i> ₃ ² (12)
<i>b</i>		<i>C</i> (4)	<i>C</i> ₃ ² (13)	<i>C</i> ₃ ² (13)
<i>c</i>			<i>C</i> (11)	<i>C</i> ₃ ² (6)
<i>d</i>				<i>C</i> (11)

Scan widths were $(1.50 + 0.30\tan\theta)^\circ$ in ω , with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. A linear decay correction was applied. The Laue group assignment, systematic absences and the absence of centrosymmetry indicated by the intensity statistics led to unique assignment of the space group as *P*2₁2₁2₁ (No. 19); since refinement proceeded well, it was adopted. Difference Fourier methods were used to locate the initial H-atom positions. Refined C—H distances range from 0.98 (2) to 1.00 (2) Å, with a mean value 0.99 Å; refined N—H and O—H distances are given in Table 2. The maximum effect of extinction is 14.3% of *F_o* for 102. The maximum peak in the final difference map occurs approximately 0.7 Å from C1; the maximum negative peak occurs roughly equidistant from C1, C2, C7 and N1.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1150). Services for accessing these data are described at the back of the journal.

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