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3-(1-Pyrrolidinyl)propanoic Acid Hemihydrate

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Abstract. $C_7H_{13}NO_2.\frac{1}{2}H_2O$, monoclinic, $P2_1/a$, $a = 11.886$ (4), $b = 10.801$ (4), $c = 12.539$ (2) Å, $\beta = 103.60$ (2)°, $Z = 8$, $D_c(140 \text{ K}) = 1.293$, $D_m(294 \text{ K}) = 1.25$ Mg m^{-3}. Final $R = 0.0485$ for 2077 observed reflections. The two independent, zwitterionic amino acid molecules form chains, roughly parallel to **b**, that are linked by alternating short [N···O = 2.649 (3) Å] and unevenly bifurcated NH···O hydrogen bonds. Adjacent chains are connected in the **a** direction by bridging water molecules. One pyrrolidine ring is unusual in that a C atom bonded to the N atom is the most puckered center.

Introduction. In a previous publication from this laboratory we noted that the N···O distance in NH···O hydrogen-bonded systems depends on both the number of hydrogen bonds from N and the formal charges on the donor and acceptor functional groups (Peterson, Hope & Nash, 1979). In particular, when an N atom having a formal positive charge and only a single functional H atom is hydrogen-bonded to a negatively charged O atom, very short N···O separations in the range 2.60 to 2.70 Å may occur. The crystal structure of the title compound was determined to obtain additional evidence bearing on the question of hydrogen-bond geometries in systems of the NH$^+$···O$^-$ type. Anhydrous 3-(1-pyrrolidinyl)-propanoic acid, PPA, was prepared by the method of Horsma & Nash (1968). Several crystals of anhydrous PPA, grown in a convection tube (Hope, 1971) using benzene–ethylene chloride mixtures as solvents, were examined and all were found to be twinned. It was established, however, that the monoclinic unit cell had at least six molecules in the asymmetric unit.

Crystals of the title compound were grown in a convection tube from the anhydrous acid and purpor-tedly anhydrous reagent-grade acetone. A crystal with dimensions 0.3 × 0.25 × 0.25 mm was mounted on a Syntex $P2_1$ diffractometer and cooled to about 140 K with a stream of cold nitrogen gas. An Mo-target X-ray tube and a graphite monochromator were used. Axial photos showed that the cell is monoclinic.

The cell and orientation parameters were determined from 16 reflections in the range $25° \le 2\theta \le 35°$. The cell dimensions (140 K; λMo $K\alpha = 0.71069$ Å) are given in the *Abstract*. The systematic absences $h0l$: h odd, and $0k0$: k odd, establish the space group $P2_1/a$.

The crystal density measured by flotation at room temperature is 1.25 Mg m^{-3}. From previous experience we would expect an increase to 1.29–1.30 Mg m^{-3} on lowering the temperature to 140 K. The calculated density is 1.216 Mg m^{-3} for eight molecules of PPA in the cell, and 1.293 Mg m^{-3} for eight PPA + four H$_2$O. The density data thus gave an early indication of the presence of water molecules in the crystal.

Intensities were measured by the ω-scan technique with scan speeds varying between 1 and 30° min^{-1} for $2\theta < 50°$. Data were collected for 2759 unique reflections, of which 2077 had intensities greater than $3\sigma(I_{net})$ and were used in refinements. The intensities of two check reflections were measured after every 120 reflections to confirm that there was no systematic drift in the system. The data were corrected for Lorentz and polarization factors but no absorption corrections were applied ($\mu = 0.104$ mm^{-1}).

The structure was solved by direct methods using a program library developed in this laboratory. Sayre's (1952) equation, as programmed by Long (1965), was used to create 16 sets of signs for the 227 reflections with $E \ge 1.70$. The set with the highest consistency index (0.890) was used to produce an E map, from

Table 1. *Fractional atomic coordinates* ($\times 10^4$ *for non-H atoms*; $\times 10^3$ *for H atoms) and isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq}/B (Å²)
C(1)	1513 (3)	5588 (3)	7840 (3)	3·7 (1)
C(2)	1925 (2)	4443 (2)	7321 (2)	2·23 (7)
C(3)	1041 (2)	3947 (2)	6351 (2)	2·09 (7)
N(4)	1403 (2)	2740 (2)	5973 (2)	1·69 (5)
C(5)	2477 (2)	2794 (3)	5530 (2)	2·13 (7)
C(6)	2310 (3)	1799 (3)	4635 (2)	2·85 (8)
C(7)	1192 (2)	1130 (3)	4699 (2)	2·46 (7)
C(8)	502 (2)	2121 (3)	5098 (2)	2·18 (7)
O(9)	587 (2)	6088 (2)	7350 (2)	5·27 (8)
O(10)	2130 (2)	5942 (2)	8740 (2)	5·34 (8)
H(21)	214 (2)	379 (2)	788 (2)	2·1 (5)
H(22)	265 (2)	465 (2)	715 (2)	1·8 (5)
H(31)	88 (2)	453 (2)	571 (2)	1·9 (5)
H(32)	30 (2)	379 (2)	655 (2)	3·1 (6)
H(4)	157 (2)	216 (2)	661 (2)	3·1 (6)
H(51)	315 (2)	265 (2)	615 (2)	1·8 (5)
H(52)	253 (2)	366 (2)	522 (2)	1·6 (5)
H(61)	298 (2)	121 (2)	478 (2)	3·2 (6)
H(62)	223 (2)	219 (2)	389 (2)	4·2 (7)
H(71)	137 (2)	42 (2)	526 (2)	2·2 (5)
H(72)	81 (2)	78 (2)	401 (2)	2·5 (5)
H(81)	−14 (2)	179 (2)	541 (2)	1·8 (5)
H(82)	19 (2)	276 (2)	454 (2)	2·2 (5)
C(1')	3974 (2)	5615 (2)	2222 (2)	1·92 (7)
C(2')	3764 (2)	4451 (3)	1506 (2)	2·41 (7)
C(3')	4872 (2)	3812 (2)	1449 (2)	2·86 (7)
N(4')	4675 (2)	2623 (2)	831 (2)	2·02 (6)
C(5')	5787 (2)	1958 (3)	820 (2)	2·65 (8)
C(6')	5759 (2)	1718 (3)	−369 (2)	2·63 (8)
C(7')	4481 (2)	1711 (3)	−918 (2)	2·81 (8)
C(8')	4015 (2)	2743 (3)	−342 (2)	2·59 (8)
O(9')	4970 (1)	6010 (2)	2551 (1)	2·41 (5)
O(10')	3066 (1)	6103 (2)	2414 (1)	2·42 (5)
H(21')	327 (2)	470 (2)	76 (2)	3·6 (6)
H(22')	326 (2)	393 (2)	179 (2)	3·0 (6)
H(31')	533 (2)	361 (2)	218 (2)	3·0 (6)
H(32')	537 (2)	434 (2)	108 (2)	2·5 (5)
H(4')	421 (3)	210 (3)	111 (2)	5·8 (9)
H(51')	577 (2)	115 (2)	123 (2)	3·0 (6)
H(52')	644 (2)	248 (3)	117 (2)	4·0 (7)
H(61')	619 (2)	93 (2)	−45 (2)	2·6 (5)
H(62')	616 (2)	240 (2)	−61 (2)	3·7 (7)
H(71')	409 (2)	92 (2)	−77 (2)	3·2 (6)
H(72')	431 (2)	183 (2)	−169 (2)	3·8 (7)
H(81')	315 (2)	270 (2)	−39 (2)	3·9 (6)
H(82')	421 (2)	358 (2)	−60 (2)	3·0 (6)
O(W)	1644 (2)	4704 (2)	3478 (2)	4·58 (8)
H(W1)	204 (3)	509 (3)	301 (3)	7·6 (11)
H(W2)	87 (3)	444 (4)	312 (3)	8·5 (12)

mizing $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F_o)$, were calculated. At this point $R = \sum ||F_o| - |F_c||/\sum |F_o|$ was 0·156. A difference Fourier map was computed and all 28 H atoms in the asymmetric unit were located. Isotropic temperature factors were assigned to the H atoms and anisotropic temperature factors were introduced for the nonhydrogen atoms. Four cycles of full-matrix least-squares refinement brought R to convergence at 0·0485.* The maximum ratio of the last shift in any atomic parameter to its e.s.d. was 0·07. A final difference Fourier map showed no significant residual electron density.

Positional parameters are listed in Table 1. Selected bond distances and bond angles are given in Table 2. Hydrogen-bonding distances and angles are given in Table 3, and torsion angles in the two pyrrolidine rings are given in Table 4.

Discussion. Fig. 1 presents both an *ORTEP* (Johnson, 1970) drawing of one of the two independent PPA molecules and a Newman projection of each molecule viewed down the appropriate C(3)—N(4) bond. Each PPA molecule is in the zwitterionic form typical of

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36839 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
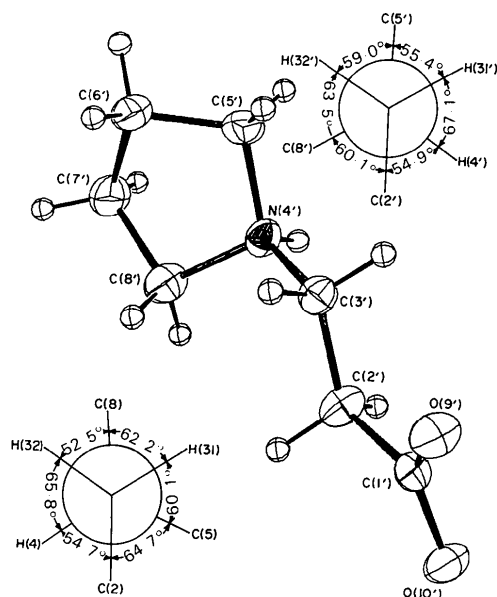

Fig. 1. The molecular conformation, atom-numbering scheme, and 50% probability ellipsoids for the primed conformer of 3-(1-pyrrolidinyl)propanoic acid. H atoms are shown as 0·1 Å radius spheres. Also given are Newman projections of both molecules down the appropriate C(3)—N(4) bond. Note the ~120° difference in the orientations of the pyrrolidine rings. E.s.d.'s on depicted angles involving H atoms are ~1·7°; otherwise ~0·3°.

which the 20 nonhydrogen atoms in the asymmetric unit containing two PPA molecules were found. There also appeared another peak which could be ascribed to the O atom of a water molecule.

Isotropic temperature factors were assigned to the 21 nonhydrogen atoms found in the E map, and four cycles of full-matrix least-squares refinement mini-

Table 2. *Bond distances (Å) and bond angles (°) with e.s.d.'s in parentheses*

C(1)—O(9)	1·250 (4)	C(1')—O(9')	1·235 (3)	O(9)—C(1)—O(10)	124·9 (3)	O(9')—C(1')—O(10')	125·6 (2)
C(1)—O(10)	1·252 (4)	C(1')—O(10')	1·274 (3)	O(9)—C(1)—C(2)	118·2 (3)	O(9')—C(1')—C(2')	119·4 (2)
C(1)—C(2)	1·531 (4)	C(1')—C(2')	1·531 (4)	O(10)—C(1)—C(2)	116·9 (3)	O(10')—C(1')—C(2')	115·0 (2)
C(2)—C(3)	1·506 (4)	C(2')—C(3')	1·503 (4)	C(1)—C(2)—C(3)	113·5 (2)	C(1')—C(2')—C(3')	112·4 (2)
C(3)—N(4)	1·485 (3)	C(3')—N(4')	1·490 (3)	C(2)—C(3)—N(4)	111·8 (2)	C(2')—C(3')—N(4')	112·8 (2)
N(4)—C(5)	1·508 (3)	N(4')—C(5')	1·507 (4)	C(3)—N(4)—C(5)	114·7 (2)	C(3')—N(4')—C(5')	112·6 (2)
C(5)—C(6)	1·533 (4)	C(5')—C(6')	1·506 (4)	C(3)—N(4)—C(8)	114·5 (2)	C(3')—N(4')—C(8')	114·7 (2)
C(6)—C(7)	1·531 (4)	C(6')—C(7')	1·513 (4)	N(4)—C(5)—C(6)	105·5 (2)	N(4')—C(5')—C(6')	106·0 (2)
C(7)—C(8)	1·504 (4)	C(7')—C(8')	1·503 (4)	C(5)—C(6)—C(7)	104·9 (2)	C(5')—C(6')—C(7')	103·7 (2)
C(8)—N(4)	1·498 (3)	C(8')—N(4')	1·501 (3)	C(6)—C(7)—C(8)	103·3 (2)	C(6')—C(7')—C(8')	102·8 (2)
N(4)—H(4)	1·00 (2)	N(4')—H(4')	0·91 (3)	C(7)—C(8)—N(4)	102·1 (2)	C(7')—C(8')—N(4')	103·9 (2)
Mean C—H	0·99 (2)	Mean C'—H'	0·99 (3)	C(8)—N(4)—C(5)	105·6 (2)	C(8')—N(4')—C(5')	106·8 (2)
O(W)—H(W1)	0·93 (4)			H(W1)—O(W)—H(W2)	114 (3)		
O(W)—H(W2)	0·97 (4)						

Table 3. *Hydrogen-bonding distances (Å) and angles (°)*

A—H⋯B	A⋯B	H⋯B	A—H⋯B
N(4)$^\mathrm{i}$—H(4)$^\mathrm{i}$⋯O(10')	2·649 (3)	1·66 (2)	174 (2)
N(4')$^\mathrm{i}$—H(4')$^\mathrm{i}$⋯O(9)	2·895 (3)	2·18 (3)	134 (2)
N(4')$^\mathrm{i}$—H(4')$^\mathrm{i}$⋯O(10)	2·954 (3)	2·07 (3)	162 (3)
O(W)—H(W2)⋯O(9)$^\mathrm{ii}$	2·746 (4)	1·79 (4)	174 (3)
O(W)—H(W1)⋯O(10')	2·825 (3)	1·91 (4)	164 (3)

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

Table 4. *Experimental pyrrolidine-ring torsion angles (°) and those calculated from equation (1) using the conformational parameters given in the text*

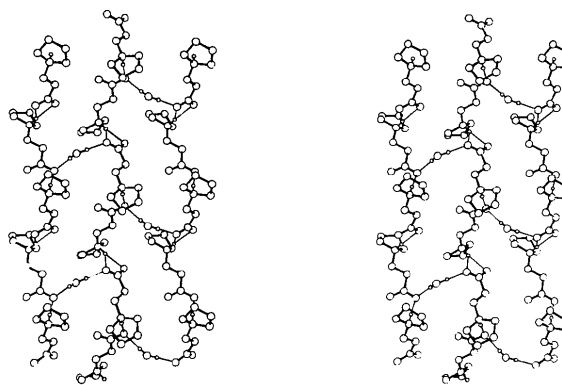|		Experimental	Calculated
χ_1	C(7)—C(6)—C(5)—N(4)	−5·8 (3)	−5·8
	C(7')—C(6')—C(5')—N(4')	−24·8 (3)	−24·8
χ_2	C(5)—C(6)—C(7)—C(8)	30·0 (3)	30·0
	C(5')—C(6')—C(7')—C(8')	39·5 (3)	39·5
χ_3	C(6)—C(7)—C(8)—N(4)	−42·7 (3)	−42·7
	C(6')—C(7')—C(8')—N(4')	−39·0 (3)	−39·0
χ_4	C(5)—N(4)—C(8)—C(7)	39·5 (3)	39·1
	C(5')—N(4')—C(8')—C(7')	23·8 (3)	23·7
χ_5	C(8)—N(4)—C(5)—C(6)	−20·7 (3)	−20·6
	C(8')—N(4')—C(5')—C(6')	0·0 (3)	0·7

Fig. 2. A stereoscopic drawing illustrating the hydrogen bonds. Only hydrogen-bonding H atoms are shown. Approximate axes: *b* up, *a* right.

most amino acids in the solid state, with the amine N and the carboxyl C in an *anti* configuration.

The independent molecules are linked by two different kinds of NH$^+$⋯O hydrogen bonds to form chains that are roughly parallel to the *b* axis of the crystal. Adjacent chains are connected in the *a*-axis direction by bridging water molecules. Fig. 2 is a stereoscopic drawing which shows the hydrogen-bonding scheme in the crystal.

Along any chain, linear N(4)—H(4)⋯O(10') hydrogen bonds alternate with unevenly bifurcated N(4')—H(4')⋯[O(9),O(10)] hydrogen bonds. The linear hydrogen bond, with an uncorrected N(4)⋯O(10') separation of 2·649 (3) Å, exemplifies

the short hydrogen bonds discussed in the *Introduction*. O(9') is not hydrogen-bonded, with the consequence that two different C—O bond lengths are present in this carboxylate group. A similar 0·04 Å disparity occurs in the C—O bond lengths of *N,N*-diethyl-*β*-alanine, which also forms singly hydrogen-bonded chains in the crystal of its benzene inclusion compound (Peterson, Hope & Nash, 1979).

The unevenly bifurcated hydrogen bond is similar to those found in α-glycine and *β*-glycine (Donohue, 1968) in that the N atom is closest to O(9) but the H atom is closest to O(10). O(9) accepts both the relatively weak hydrogen bond from N and a second hydrogen bond from the bridging water molecule, with the result that in this carboxylate group the two C—O bond lengths are virtually identical. Moreover, the mean C—O bond length is, within experimental uncertainty, the same as that found in neutron diffraction studies of 13 amino acids (Koetzle & Lehmann, 1976).

It is evident in Fig. 2 that the water molecule is well removed from the planes of either of the carboxylate acceptor groups. The perpendicular distance from O(W) to the C(1), C(2), O(9), O(10) least-squares

plane is 1·566 Å. The vector O(W)—O(9) is inclined to this plane by 34·8°. O(W) is out of the C(1'), C(2'), O(9'), O(10') least-squares plane by a perpendicular distance of 2·090 Å, and the angle of inclination of the O(W)—O(10') vector to this plane is 47·7°. In their recent survey of OH···O hydrogen-bond geometries, Mitra & Ramakrishnan (1977) report that angles of inclination in the range 30–50° were found in only 12 out of 77 cases involving hydrogen bonds to carbonyl groups.

The two pyrrolidine rings have different conformations which can be described quite successfully using the conformational equations of DeTar & Luthra (1977). According to these authors, the ith torsional angle in a five-membered ring is given by the equation

$$\chi_i = a_o \cos [t + 4\pi(i - 2)/5], \qquad (1)$$

where a_o is the puckering amplitude and t is a phase angle. Envelope conformations occur when $t = 18, 54°$, etc., while half-chair conformations occur when $t = 0, 36, 72°$, etc. DeTar & Luthra have tabulated the values of a_o, t, and the additional parameter $d_1 = (\chi_3 - \chi_2)/2$, for the pyrrolidine rings in 40 proline derivatives.

In the present instance the 'primed' pyrrolidine ring has $a_o = 41·3°$, $t = 17·0°$, and $d_1 = -7·1°$. It is an almost perfect envelope with C(7') as the flap. The other four atoms in the ring are coplanar to within ±0·004 Å, with C(7') out of the plane by 0·60 Å on the same side as H(4').

The pyrrolidine ring in the 'unprimed' conformer, with parameters $a_o = 43·4°$, $t = 46·3°$, and $d_1 = -18·45°$, is relatively unusual in that the most puckered center is a C atom bonded to the N. This behavior was shown by only two of the 40 rings characterized by DeTar & Luthra. C(8) is 0·51 Å out of the N(4), C(5), C(6) plane, on the same side as C(3), while C(7) is only 0·15 Å out of this plane on the opposite side.

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N-(o-Bromophenyl)-o-bromobenzylamine

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Abstract. $C_{13}H_{11}Br_2N$, $M_r = 341·06$, triclinic, $P\bar{1}$, $a = 10·930$ (2), $b = 11·291$ (9), $c = 10·749$ (2) Å, $\alpha = 108·10$ (3), $\beta = 92·83$ (2), $\gamma = 85·25$ (4)°, $V = 1256$ (2) Å³, $Z = 4$, $D_c = 1·803$ g cm⁻³. The structure was solved by heavy-atom techniques and refined by least squares, using 2241 observed data with $F_o > 3\sigma(F_o)$, and anisotropic temperature factors, to $R_w = 0·031$ and $R = 0·044$. The two halves of each of the two molecules in the asymmetric unit are rotated about the central C—N bond to make dihedral angles of 79·0 and 76·9°. The average Br—C distance is 1·894 (8) Å and the average C—C (ring) distance is 1·379 (12) Å.

Introduction. Many tricyclic compounds show psychotropic activity (Chang, 1979). Useful precursors to these potential drugs contain *o*-bromo-substituted phenyl rings separated by one or more atoms (Chang, 1979). These latter materials provide a vehicle for the