

Fig. 1. The atomic numbering scheme used.

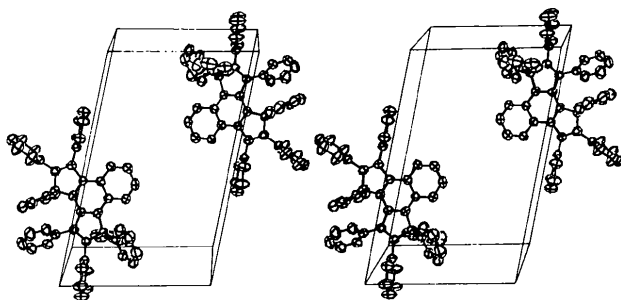


Fig. 2. A stereoscopic diagram of the contents of one unit cell.

and K, which are connected to the nucleus by sp^2-sp^2 bonds, make large dihedral angles, in the range $59-86^\circ$, with the five-membered rings to which they are bonded (Figs. 1 and 2).

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D,L-3-Amino-1-hydroxy-2-pyrrolidone Trihydrate (D,L-HA-966)

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Abstract. $C_4H_8N_2O_2 \cdot 3H_2O$, $M_r = 170.2$, monoclinic, $P2_1/c$, $a = 11.86$ (8), $b = 6.84$ (14), $c = 11.73$ (14) Å, $\beta = 114.94$ (2)°, $U = 863$ Å³, $D_x = 1.31$ Mg m⁻³, $Z = 4$; final $R = 0.056$ for 977 unique reflections. The compound exists as a zwitterion in the crystal. The pyrrolidine ring has an almost perfect envelope

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In the naphthalene system the distances in ring A are very close to those measured and calculated by molecular-orbital methods in naphthalene itself (Cruikshank & Sparks, 1960). However, in ring B the bond character appears to be modified by fusion with the five-membered rings. Throughout the rest of the molecule bond distances and angles, other than those noted above, appear normal.

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conformation and very little hydrogen bonding occurs between the water molecules and the HA-966 molecules.

Introduction. The title compound has been reported as a selective antagonist at the physiological aspartate

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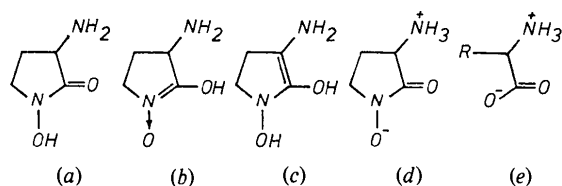


Fig. 1. (a)–(d) Possible tautomers of D,L-HA-966 after Davies & Watkins (1973). Also, for comparison, the α -amino acid moiety of L-aspartate (e) where R is CH_2COOH .

receptor in the vertebrate central nervous system (Biscoe, Davies, Dray, Evans, Francis, Martin & Watkins, 1977). It has been suggested (Davies & Watkins, 1973) that it may exist in one of several different tautomeric forms (Fig. 1), only one of which (Fig. 1d) would sterically allow its potential interaction with the aspartate receptor. The present structure determination was undertaken to determine which tautomer was present in that sample of D,L-HA-966 assayed in previous radioligand-receptor binding experiments (Derricott & Steward, 1980).

Transparent elongated-tabular monoclinic crystals were grown from aqueous solution and a crystal $0.3 \times 0.2 \times 0.4$ mm was encapsulated in a silica-glass capillary tube containing a saturated solution of the compound. This mounting method was adopted since the crystals effloresced rapidly when exposed to air. As a result of this rapid water loss the density of the crystals could not be measured accurately. Data were collected photographically on Weissenberg film packs, each containing four films, with Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Levels $h0l$ to $h6l$ were collected and also the $hk0$ level in order to obtain inter-level scale factors. The films were processed by the SRC Microdensitometer Service (Daresbury Laboratory, Daresbury, Warrington WA4 4AD, Cheshire) to yield structure factor data and a non-linear least-squares refinement of the cell dimensions. Lp corrections were applied but no absorption corrections [$\mu(\text{Cu } K\alpha) = 0.936 \text{ mm}^{-1}$] were made; 977 unique reflexions were used in the refinement.

The systematic absences $h0l, l = 2n + 1$ and $0k0, k = 2n + 1$ uniquely defined the space group $P2_1/c$.

The structure was solved by direct methods (SHELX 76, Sheldrick, 1976). All the non-H atoms in the asymmetric unit, except for the water O atoms, were revealed by an E map calculated with 168 reflexions ($E \geq 1.2$). Isotropic full-matrix least-squares refinement ($R = 0.40$) followed by a difference synthesis revealed two of the three water O atoms and also two H atoms. Further isotropic refinement ($R = 0.25$) revealed the third water O atom and the remaining H atoms were located after further anisotropic refinement. The H atoms bonded to the waters O(4) and O(5) were difficult to locate as a consequence of three or four peaks appearing, in a

difference synthesis, proximal to each O atom. Those peaks which formed a dimensionally reasonable hydrogen-bond network were chosen as the most likely candidates and this was justified by their subsequent satisfactory refinement; the other peaks did not refine. The appearance of these spurious peaks may indicate a degree of disorder, although a disordered model, with fractional site-occupation factors, was unsuccessfully tried. H atoms bonded to C were included in calculated positions (C–H 1.08 \AA , H–C–H 109.5°) and refined with a riding model in which C–H vectors were constant in magnitude and direction but not position. N–H and O–H lengths were constrained

Table 1. Final fractional atomic coordinates ($\times 10^4$)

	x	y	z
N(1)	1532 (3)	5391 (4)	1239 (2)
C(2)	1046 (3)	7075 (5)	786 (3)
C(3)	1479 (3)	7646 (6)	–204 (3)
C(4)	2089 (4)	5811 (7)	–412 (4)
C(5)	2322 (4)	4532 (6)	710 (4)
N(2)	408 (3)	8307 (4)	–1361 (3)
O(1)	1374 (2)	4525 (4)	2212 (2)
O(2)	337 (3)	8024 (4)	1110 (2)
H(1)*	2123 (3)	8858 (6)	72 (3)
H(2)	–242 (36)	7218 (56)	–1682 (46)
H(3)	721 (42)	8716 (73)	–2006 (35)
H(4)	83 (45)	9588 (45)	–1179 (47)
H(5)*	2954 (4)	6166 (7)	–461 (4)
H(6)*	1478 (4)	5087 (7)	–1268 (4)
H(7)*	3287 (4)	4581 (6)	1373 (4)
H(8)*	2058 (4)	3037 (6)	426 (4)
O(3)	3531 (3)	3135 (5)	3834 (3)
H(9)	3679 (47)	1815 (39)	3666 (49)
H(10)	2737 (27)	3597 (74)	3287 (40)
O(4)	4964 (3)	6271 (5)	3688 (3)
H(11)	4519 (52)	5097 (57)	3708 (59)
H(12)	5482 (39)	6454 (80)	4557 (21)
O(5)	3756 (4)	–200 (6)	2633 (4)
H(13)	4016 (56)	–1530 (40)	2832 (59)
H(14)	4319 (47)	404 (91)	2364 (56)

* Atoms in calculated positions.

Table 2. Torsion angles ($^\circ$) involving non-hydrogen atoms

The sign convention is as defined by Klyne & Prelog (1960).

C(5)–N(1)–C(2)–C(3)	0.0 (4)
C(5)–N(1)–C(2)–O(2)	179.2 (3)
O(1)–N(1)–C(2)–C(3)	176.1 (3)
O(1)–N(1)–C(2)–O(2)	–4.7 (5)
C(2)–N(1)–C(5)–C(4)	–10.8 (4)
O(1)–N(1)–C(5)–C(4)	173.1 (3)
N(1)–C(2)–C(3)–C(4)	70.8 (4)
N(1)–C(2)–C(3)–N(2)	132.2 (3)
O(2)–C(2)–C(3)–C(4)	–168.4 (4)
O(2)–C(2)–C(3)–N(2)	–47.1 (5)
C(2)–C(3)–C(4)–C(5)	–16.8 (4)
N(2)–C(3)–C(4)–C(5)	–136.4 (3)
C(3)–C(4)–C(5)–N(1)	16.4 (4)

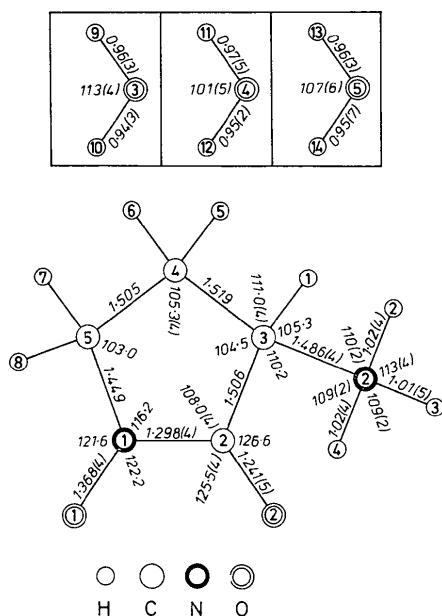


Fig. 2. Atomic numbering scheme, bond lengths (Å) and angles ($^{\circ}$) for D,L-HA-966. E.s.d.'s are 0.006 Å for bonds and 0.3 $^{\circ}$ for angles except where indicated otherwise. Bond angles not included on the figure are: N(2)–C(3)–C(4) 112.7, C(3)–N(2)–H(3) 109.2 $^{\circ}$.

(± 0.02 Å) at 1.02 and 0.96 Å respectively. A common isotropic temperature factor [0.086 (5) Å 2] was refined for all H atoms except for those bonded to the waters O(4) and O(5). A larger common isotropic temperature factor [0.12 (1) Å 2] was refined for the latter, not inconsistent with the possible disorder mentioned earlier. Two strong reflexions exhibiting extinction were omitted from the final refinement which then converged to $R = 0.056$ for 130 parameters.

Final atomic coordinates are given in Table 1 and the torsion angles involving non-H atoms in Table 2. The molecular geometry is illustrated in Fig. 2.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35223 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

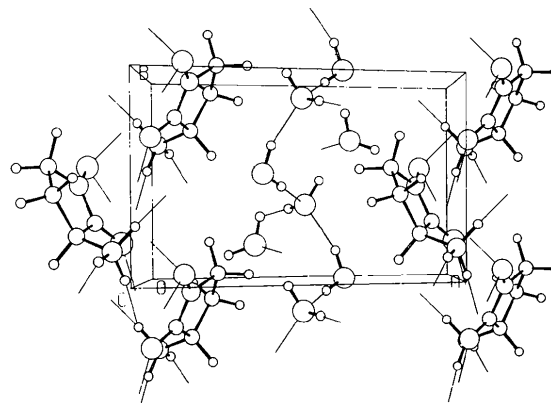


Fig. 3. Crystal packing diagram projected along c .

Discussion. HA-966 exists, in the crystal, as that tautomer (Fig. 1*d*) which is the most similar to the α -amino acid region of L-aspartate (Fig. 1*e*). This may support the contention (Biscoe *et al.*, 1977) that HA-966 may act as a direct antagonist at the physiological aspartate receptor.

In common with L-aspartate (Thyagaraja Rao, Srinivasan & Valambal, 1968; Derissen, Endeman & Peerdeman, 1968), HA-966 exists as a zwitterion in the crystal where the N(2) amino group is protonated and the O(1) hydroxyl group deprotonated. A degree of electron resonance around the N(1), C(2), O(2) portion of the molecule is reflected in the bond lengths: C(2)–O(2) is slightly longer than a normal double bond (Pople & Beveridge, 1970) whilst N(1)–C(2) is shorter than expected. The H atoms of the ammonium group adopt a staggered conformation [C(4)–C(3)–N(2)–H(2) 58.4 $^{\circ}$].

The pyrrolidine ring of HA-966 has an almost perfect C(4) envelope conformation where C(4) lies 0.31 Å from the C(2), O(2), N(1) plane; C(3) and C(5) both deviate from this by only 0.02 Å. Many other substituted 2-pyrrolidones adopt similar ring conformations (Dupont, Dideberg & Welter, 1975; Aubry, Marraud, Protas & Néel, 1972; Ball, Desiderato & Freeman, 1973; Molin-Case, Fleischer & Urry, 1970).

The packing is illustrated in Fig. 3 and the geometry of the intermolecular hydrogen bonding is given in

Table 3. Hydrogen-bond lengths (Å) and angles ($^{\circ}$)

A–H...B	Symmetry of acceptor	A–H	H...B	A...B	\angle A–H...B
N(2)–H(2)...O(1)	$-x, 1-y, -z$	1.02 (4)	1.70 (4)	2.727 (4)	180 (24)
N(2)–H(3)...O(1)	$x, \frac{1}{2}-y, z-\frac{1}{2}$	1.01 (5)	1.87 (5)	2.815 (4)	154 (14)
N(2)–H(4)...O(2)	$-x, 2-y, -z$	1.02 (4)	1.72 (4)	2.718 (4)	166 (18)
O(3)–H(9)...O(5)	x, y, z	0.96 (3)	1.86 (3)	2.813 (6)	170 (16)
O(3)–H(10)...O(2)	x, y, z	0.94 (3)	1.70 (3)	2.639 (4)	180 (25)
O(4)–H(11)...O(3)	x, y, z	0.97 (5)	1.83 (5)	2.787 (5)	170 (24)
O(4)–H(12)...O(3)	$1-x, 1-y, 1-z$	0.95 (2)	1.77 (2)	2.724 (5)	180 (19)
O(5)–H(13)...O(4)	$x, y-1, z$	0.96 (3)	1.89 (3)	2.813 (6)	160 (10)
O(5)–H(14)...O(4)	$1-x, y-\frac{1}{2}, \frac{1}{2}-z$	0.95 (7)	1.87 (7)	2.775 (6)	160 (23)

Table 3. Although there is extensive hydrogen bonding between the water molecules (Fig. 3) and also between the HA-966 molecules (Table 3) there is only a single hydrogen bond [O(3)—H(10)···O(2)] linking the water molecules with the HA-966 molecules. This may explain the highly efflorescent nature of the crystals. Two of the three water molecules of the asymmetric unit furnish four hydrogen bonds, in common with ordinary ice (Pauling, 1960), and O(2) of the HA-966 molecule furnishes two hydrogen bonds.

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Structure of Dimethyl 4,4'-Methylenebis(phenylcarbamate): a Model for MDI Units in Polyurethane Hard Segments

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Abstract. $C_{17}H_{18}N_2O_4$, monoclinic, $P2_1/b$, $a = 5.157$ (3), $b = 9.800$ (3), $c = 31.472$ (11) Å, $\gamma = 93.90$ (3)°, $Z = 4$, $D_m = 1.30$, $D_c = 1.316$ Mg m⁻³. The structure was refined to $R = 0.06$ based on diffractometer data collected at 258 K. The molecule is V-shaped with a C—CH₂—C angle of 114.5 (4)°. The angle between the phenyl-ring planes is 90.0° and the planes of the urethane groups are at angles of 10.2 and 39.4° to their adjacent phenyl rings. The molecules are linked into sheets by C=O···H—N hydrogen bonds between the urethane groups. The title compound furnishes a conformational model for the diol-linked 4,4'-methylenebis(phenyl diisocyanate) units in the hard segments of certain polyurethane elastomers.

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Introduction. Polyurethane elastomers are block copolymers composed of alternating hard (urethane) and soft (polyester or polyether) segments. The elastomeric properties of these materials are attributed to microphase separation: the urethane segments segregate to form crystalline domains which serve as crosslinks between the soft-segment chains. One commercially important polyurethane system has hard segments composed of diol-linked 4,4'-methylenebis(phenyl diisocyanate) (MDI). The structure of the hard domains has not been determined by direct study of the polymer, due to the low quality of the X-ray diffraction data, but it is believed that hydrogen bonding between the urethane groups is an important factor in the virtual (non-covalent) crosslinking of the chains (Bonart, Morbitzer & Muller, 1974). The title compound is methanol-capped MDI, and its structure has been determined as a model for the structure of the polymer system.