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A 1:1 molecular complex of 4-aminocyclohexanol and (4-hydroxycyclohexyl)carbamic acid

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.037
wR factor = 0.102
Data-to-parameter ratio = 12.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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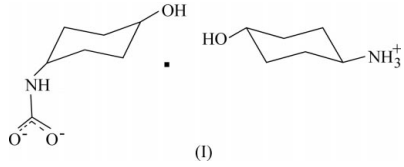
The title molecular complex, 4-ammoniocyclohexanol (4-hydroxycyclohexyl)carbamate, $C_6H_{14}NO^+\cdot C_7H_{12}NO_3^-$, forms an ionic column with N—H···O, O—H···O and C—H···O interactions. There are two different cyclic supramolecular synthons of note. The crystal structures of ionic amino acids also have similar structural patterns.

Comment

The title molecular complex, (I), was obtained during a study of 4-aminocyclohexanol. This type of compound has a tendency to form carbonated adducts by reaction with atmospheric CO_2. In this regard, the crystal structure of 2-aminocyclohexylcarbamate has been reported (Hanessian *et al.*, 1995). In our case, 4-hydroxycyclohexylcarbamic acid initially formed, then crystallized with the original 4-aminocyclohexanol to give a 1:1 ionic molecular complex with proton transfer.



(I)

The molecular structure and atom numbering are given in Fig. 1. The main features are similar to those in the molecular complex of methyl 3-acetoxy-1-ammonio-4-iodocyclohexane-1-carboxylate and trifluoroacetate (Avenoza *et al.*, 1997) and similar to 2-aminocyclohexylcarbamate (Hanessian *et al.*, 1995). The ions form a columnar arrangement with several N—H···O interactions (Table 1); the packing is shown in Fig. 2. Weak C—H···O interactions (Table 1) reinforce the

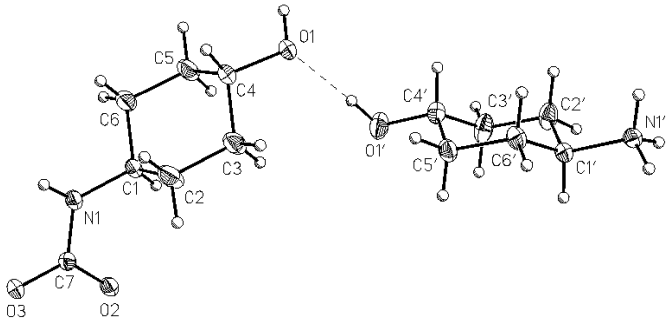


Figure 1
A view of the molecular structure of the title complex, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

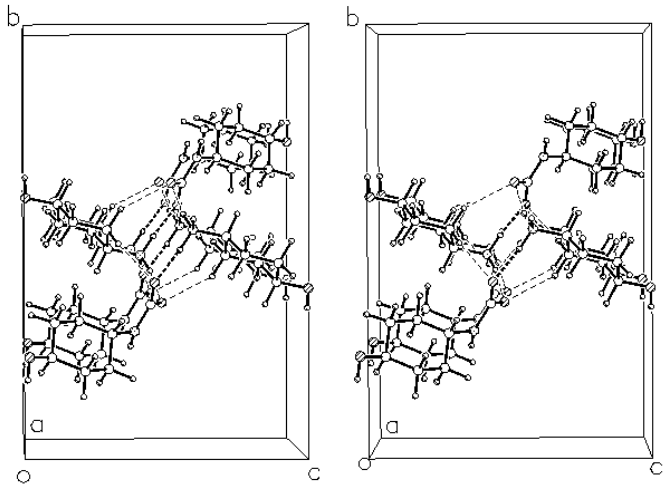


Figure 2
Stereoview of the columnar packing, viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

column formation. A closer view of the columnar packing shows that it is composed of two cyclic supramolecular synthons A and B (Fig. 3). Both types of synthon are observed in other ionic amino acids. In the Cambridge Structural Database (Version 5.24, July 2003; Allen, 2002), the crystal structures with refcodes ACXTPY (Bhattacharjee *et al.*, 1975), ACYHXA01 (Valle *et al.*, 1988), DMTYRS (Gaudestad *et al.*, 1976), FOBJUB (Pirrung, 1987), MEMTYR10 (Satyshur & Rao, 1983) RIGSEF (Avenoza *et al.*, 1997) and TOKNUC (Allan *et al.*, 1996) contain synthons A and B.

O—H···O(carboxylate) and O—H···O(hydroxyl) hydrogen bonds act as connectors between the columns.

Experimental

Neutralization of the commercially available (Lancaster) hydrochloride salt of 4-aminocyclohexanol by $NaHCO_3$ in water affords the 4-aminocyclohexanol (extracted with EtOAc). The compound crystallized from a 1:1:1 mixture of EtOAc, CH_3CN and EtOH. During the time of crystallization, 4-aminocyclohexanol is carboxylated by atmospheric CO_2 to give the carbamic acid which cocrystallizes with the parent compound to give yellow crystals of the 1:1 molecular complex.

Crystal data

$C_6H_{14}NO^+\cdot C_7H_{12}NO_3^-$
M_r = 274.36
Monoclinic, $P2_1/c$
a = 6.3452 (2) Å
b = 18.6256 (6) Å
c = 12.1664 (4) Å
β = 92.284 (2)°
V = 1436.72 (8) Å^3
Z = 4
D_x = 1.268 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4934 reflections
θ = 2.8–27.5°
μ = 0.09 mm^{-1}
T = 120 (2) K
Plate, yellow
0.22 × 0.12 × 0.04 mm

Data collection

SMART 6K CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.927, T_{max} = 1.000
19783 measured reflections
3308 independent reflections
2537 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 27.5°
$h = -7 \rightarrow 8$
$k = -24 \rightarrow 24$
$l = -15 \rightarrow 15$

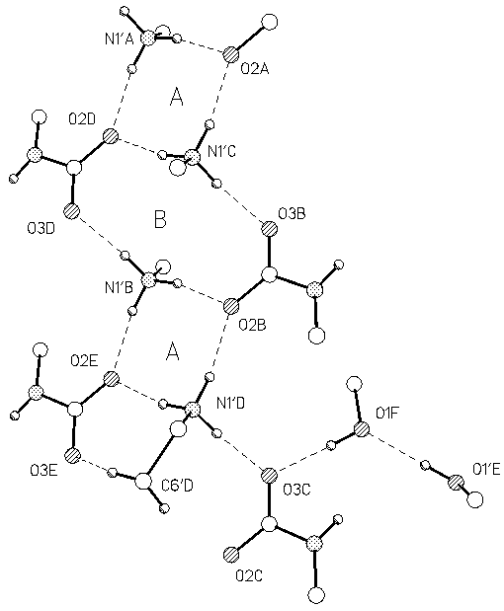


Figure 3
Segment of the crystal structure, showing synthons A and B.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.102
S = 1.01
3308 reflections
276 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2 + 0.3252P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1′—H1′···O1	0.90 (2)	1.88 (2)	2.784 (2)	176 (1)
O1—H1···O3^{i}	0.90 (2)	1.79 (2)	2.687 (1)	175 (2)
N1′—H111···O2^{ii}	0.94 (2)	1.90 (2)	2.816 (1)	167 (1)
N1′—H112···O3^{iii}	0.95 (2)	1.82 (2)	2.7590 (1)	170 (1)
N1′—H114···O2^{iv}	0.92 (2)	1.87 (2)	2.7870 (1)	169 (1)
C6′—H6D···O3^{ii}	0.96 (2)	2.54 (1)	3.417 (1)	152 (1)

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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