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N-Propionylhydroxylamine forms a three-dimensional hydrogen-bonded framework structure

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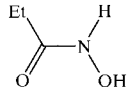
The title compound, *N*-hydroxypropanamide, $C_3H_7NO_2$, crystallizes with $Z' = 3$ in $P2_1/c$. The molecules are linked by three N—H···O hydrogen bonds [N···O 2.8012 (16) to 2.8958 (15) Å; N—H···O 163 to 168°] and by three O—H···O hydrogen bonds [O···O 2.6589 (15) to 2.6775 (17) Å; O—H···O 165 to 177°] into a single three-dimensional framework.

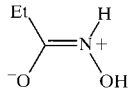
Comment

Simple carboxylic amides RCONH$_2$ exhibit a wide variety of supramolecular arrangements, even though each molecule generally acts as a twofold donor and as a twofold acceptor of hydrogen bonds (Leiserowitz & Schmidt, 1969). Thus, for example, the orthorhombic polymorph of acetamide, CH_3CONH_2 [Cambridge Structural Database (Allen & Kennard, 1993) code ACEMID; Hamilton, 1965] forms one-dimensional ribbons, as does benzamide, PhCONH$_2$ (BZAMID01; Blake & Small, 1972), whereas the rhombohedral polymorph of acetamide (ACEMID01; Denne & Small, 1971) forms a three-dimensional array. Propionamide $C_2H_5CONH_2$ (ZZZKAY01; Usanmaz & Adler, 1982), by contrast, forms a two-dimensional hydrogen-bonded structure. Despite this wide variety, the hydrogen-bonding behaviour of the hydroxylated analogues, the *N*-acylhydroxylamines RCONHOH, has been much less intensively studied. The structure of MeCONHOH has been reported (ACXMAC; Bracher & Small, 1970), but only as the hemihydrate, where the intrinsic behaviour of the hydroxylamine itself is obscured. Accordingly, we have now investigated the supramolecular structure of anhydrous *N*-propionoylhydroxylamine, $C_2H_5CONHOH$, (I).

Compound (I) crystallizes in space group $P2_1/c$ with three independent molecules in the asymmetric unit (Fig. 1). The hydrogen-bonding behaviour (Table 1) and the molecular conformations (Table 2) of these molecules preclude the possibility of any additional symmetry. Each molecule acts as a twofold donor of hydrogen bonds, one each of the N—H···O and O—H···O types, and each acts as a twofold acceptor (Table 1): each molecule of type 1 (containing N1) accepts one hydrogen bond from a type 2 molecule (containing N2) and one from a type 3 molecule (containing N3); each molecule of type 2 accepts hydrogen bonds from two different type 1 molecules; and each type 3 molecule accepts one hydrogen bond from a type 2 molecule and one from another type 3 molecule.



(I)



(I*a*)

In each of the independent molecules, the C—C(O)—N(H)—O moiety is nearly planar with the central O—C—N—H unit in a *trans* conformation. The C—O bonds in (I) are all at the upper end of the range typically found in simple amides of type RCONH$_2$ [mean 1.234 (12) Å; upper quartile 1.243 Å (Allen *et al.*, 1987)], and the C—N bonds are at the lower end of the range of such bonds in these amides [mean 1.325 (9) Å; lower quartile 1.318 Å]. This suggests that the canonical form (I*a*) is significant here regardless of the presence of the *N*-hydroxy group. The N—O bond lengths are unexceptional. Consistent with the importance of (I*a*), the sole hydrogen-bond acceptors in (I) are the carbonyl O atoms: the hydroxyl O and the N atoms are donors only. Each carbonyl group and its two associated hydrogen-bond donors, one O and one N, form an almost planar array (Table 3); the angle sums around these O acceptors are all close to 360°. However, it is notable that the angles involving the N donors are consistently and significantly wider than those involving the O donors.

Within the selected asymmetric unit (Fig. 1), atoms O22 and N3 both act as hydrogen-bond donors to O11. The remaining four hydrogen bonds, two each of the N—H···O and O—H···O types, link these three-molecule units into a single three-dimensional framework. This framework is most easily analysed in terms of three distinct one-dimensional motifs, running parallel to the [010], [001] and [100] directions, and utilizing one, two and three types of molecule, respectively.

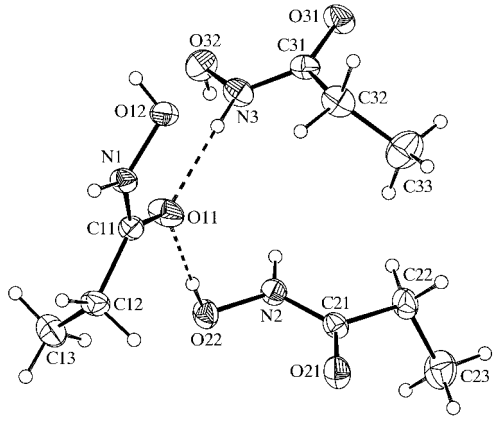


Figure 1
The three independent molecules in (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Firstly, atom O32 in the asymmetric unit at (x, y, z) acts as hydrogen-bond donor to O31 at $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$, while O32 at $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$ in turn acts as donor to O31 at $(x, 1+y, z)$, so producing a $C(5)$ chain running parallel to the [010] direction, involving only a single type of molecule and generated by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{1}{4})$ (Fig. 2). Secondly, O12 at (x, y, z) acts as donor to O21 at $(x, \frac{1}{2}-y, \frac{1}{2}+z)$, while O12 at $(x, \frac{1}{2}-y, \frac{1}{2}+z)$ acts as donor to O21 at $(x, y, 1+z)$, producing a $C_2^2(10)$ chain parallel to [001], involving molecules of types 1 and 2 and generated by the glide plane at $y = \frac{1}{4}$ (Fig. 3). Finally, N2 at (x, y, z) acts as donor to O31 at $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$, while N1 at $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$ acts as donor to O21 at $(1+x, y, z)$, thus generating a $C_3^3(12)$ chain running parallel to [100] and involving all three independent molecules (Figs. 2 and 3).

The pairwise combinations of these three chain motifs give rise to three intersecting two-dimensional arrays which together make up the overall three-dimensional framework. Thus, for example, the combination of the [100] and [001] motifs generates an (010) net built from centrosymmetric $R_{10}^8(38)$ rings involving all three types of molecule (Fig. 3), while the combination of the [100] and [010] chain motifs produces an (001) net built from $R_{10}^9(40)$ rings (Fig. 2)

In the hemihydrate of the *N*-acetyl analogue of (I) (ACXMAC; Bracher & Small, 1970), there is only one independent molecule of the hydroxylamine, which again acts as a double donor of hydrogen bonds and as a double acceptor with only the carbonyl O acting as acceptor. The molecules are linked by N—H···O hydrogen bonds into $C(4)$ chains, two per unit cell. The water molecules, which lie on twofold rotation axes in *Pnn*2, act as double donors and as double acceptors in O—H···O hydrogen bonds; each water molecule is thereby linked to four different $C(4)$ chains and these links serve to connect all of the molecules into a single three-dimensional framework.

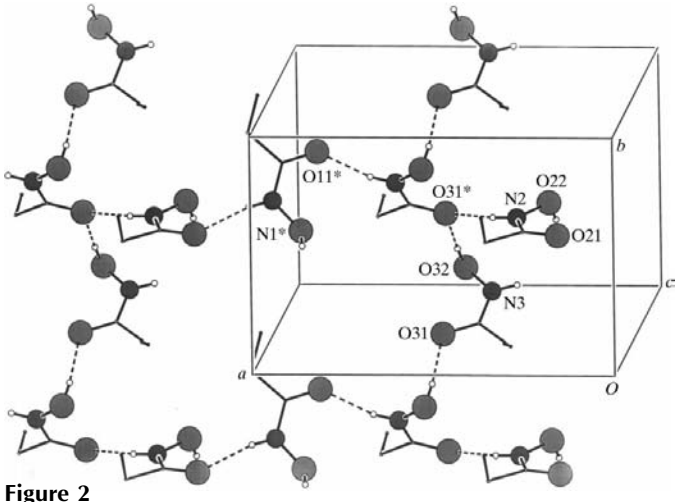


Figure 2
Part of the crystal structure of (I) showing $C(5)$ and $C_3^3(12)$ chains parallel to [010] and [100], respectively, combining to form a (001) sheet of $R_{10}^9(40)$ rings. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$.

By contrast to the rather complex three-dimensional structures in both (I) and ACXMAC, the sulfonylhydroxylamine analogues $MeSO_2NHOH$ (DIRMIA; Brink & Mattes, 1986) and $PhSO_2NHOH$ (JEHWUO; Scholz *et al.*, 1989) form much simpler supramolecular structures. In both compounds, the N—H and O—H units act as hydrogen-bond donors, as in the acylhydroxylamines, but each of the sulfonyl O atoms acts as a single acceptor. The molecules in DIRMIA are linked thus into molecular ladders with pairs of antiparallel $C_2^2(7)$ uprights enclosing centrosymmetric $R_2^2(10)$ rings between the S—N bonds acting as rungs; in JEHWUO, the molecules are linked into (4,4) nets (Batten & Robson, 1998) built from a single type of $R_4^4(16)$ ring.

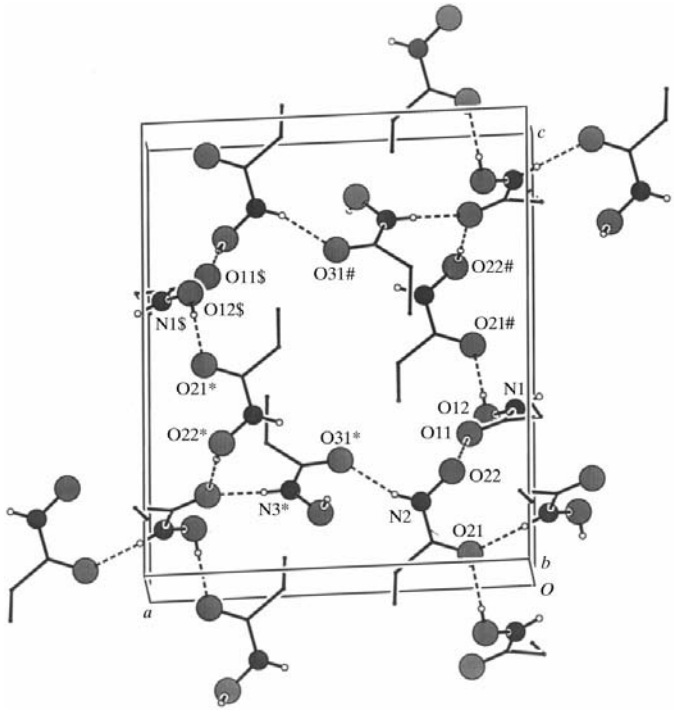


Figure 3
Part of the crystal structure of (I) showing $C_2^2(10)$ and $C_3^3(12)$ chains parallel to [001] and [100], respectively, combining to form a (010) sheet of $R_{10}^8(38)$ rings. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$, $(x, \frac{1}{2}-y, \frac{1}{2}+z)$ and $(1-x, 1-y, 1-z)$, respectively.

Experimental

Crystals of (I) suitable for single-crystal X-ray diffraction were provided by Professor D. A. Brown of University College Dublin. A synthesis is described in Brown & Roche (1983).

Crystal data

$C_3H_7NO_2$
$M_r = 89.10$
Monoclinic, $P2_1/c$
$a = 12.052\ (3)$ Å
$b = 8.009\ (3)$ Å
$c = 14.354\ (3)$ Å
$\beta = 92.35\ (2)^\circ$
$V = 1384.3\ (7)$ Å^3
$Z = 12$
$D_x = 1.282$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.81$–11.23°
$\mu = 0.107$ mm^{-1}
$T = 293\ (2)$ K
Block, colourless
0.40 × 0.40 × 0.40 mm

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
3374 measured reflections
3016 independent reflections
2426 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 26.97^\circ$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 10$
$l = -18 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.114$
$S = 1.020$
3016 reflections
170 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2 + 0.3743P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.026 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
O12—H12···O21^{i}	0.82	1.84	2.6589 (15)	175
N1—H1···O21^{ii}	0.86	2.05	2.8958 (15)	166
O22—H22···O11	0.82	1.84	2.6624 (16)	177
N2—H2···O31^{iii}	0.86	2.03	2.8609 (16)	163
O32—H32···O31^{iii}	0.82	1.88	2.6775 (17)	165
N3—H3···O11	0.86	1.95	2.8012 (16)	168

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

Table 2
Selected geometric parameters (Å,°).

Parameter	$n = 1$	$n = 2$	$n = 3$
On1—Cn1	1.2414 (15)	1.2435 (15)	1.2472 (16)
Cn1—Nn	1.3103 (18)	1.3121 (17)	1.3117 (19)
Nn—On2	1.3887 (15)	1.3872 (14)	1.3854 (15)
On1—Cn1—Nn—On2	−8.5 (2)	−6.6 (2)	−1.6 (2)
Nn—Cn1—Cn2—Cn3	134.74 (14)	−118.96 (16)	111.78 (17)

Compound (I) crystallized in the monoclinic system; space group $P2_1/c$ was assumed from the systematic absences. All H atoms were clearly revealed in difference maps and were then allowed for as riding atoms, with C—H = 0.96 (CH_3) or 0.97 Å (CH_2), N—H = 0.86 Å and O—H = 0.82 Å.

Table 3
Angles (°) around the carbonyl-O acceptor sites.

Parameter	$n = 1$	$n = 2$	$n = 3$
Cn1—On1···O†	124.01 (9)	116.47 (9)	118.34 (10)
Cn1—On1···N†	140.71 (10)	133.14 (9)	138.13 (10)
O···On1···N	95.06 (5)	110.36 (5)	99.39 (5)

† O and N donors are defined in Table 1.

Data collection: *CAD*-4-*PC Software* (Nonius, 1992); cell refinement: *SET*4 and *CELDIM* (Nonius, 1992); data reduction: *HELENA* in *PLATON* (Spek, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1449). Services for accessing these data are described at the back of the journal.

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