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Two substituted 2-pyrrolin-5-ones: chains built from a single N—H···O hydrogen bond

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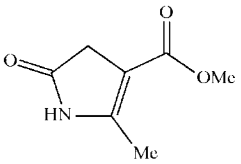
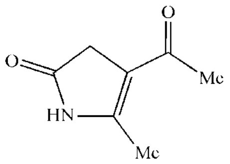
In each of methyl 2-methyl-5-oxo-2-pyrroline-3-carboxylate, $C_7H_9NO_3$, and 3-acetyl-2-methyl-2-pyrrolin-5-one, $C_7H_9NO_2$, the pyrrolinone ring is planar. In each structure, molecules are linked into simple chains by way of a single N—H···O hydrogen bond.

Comment

As precursors for the synthesis of pyrrole derivatives, 2-pyrrolin-5-one derivatives have been prepared by the reaction of glyoxal with enaminoesters (San Feliciano *et al.*, 1989). However, pyrrolinones accessible by this method are few in number. We report here the structures of two such compounds, namely 2-methyl-3-methoxycarbonyl-2-pyrrolin-5-one, (I), and 2-methyl-3-acetyl-2-pyrrolin-5-one, (II) (Figs. 1 and 2).



(I)



(II)

In each molecule, the five-membered ring (N1/C1–C4) is planar, with r.m.s deviations from the mean plane of 0.007 Å for (I) and 0.006 Å for (II). Within the pyrrolinone rings in (I) and (II), the bond distances provide evidence for π-conjugation and are different from those in substituted ethylenedi(2-pyrrolin-5-one) (Zhang *et al.*, 2007). The N1—C2 and N1—C5 bonds [1.391 (2) and 1.359 (2) Å, respectively, for (I), and 1.396 (2) and 1.358 (2) Å for (II)] are shorter than the corresponding bonds in ethylenedi(2-pyrrolin-5-one) (1.411 and 1.385 Å, respectively). Conversely, the C2—C3 bond becomes longer [1.385 and 1.411 Å in (I) and (II), respectively, *versus* 1.349 Å in ethylenedi(2-pyrrolin-5-one)]. This indicates that the lone pair of electrons on atom N1 and the π electrons of C2═C3 in (I) and (II) exhibit significant delocalization compared with ethylenedi(2-pyrrolin-5-one).

In (I), the exocyclic bond angles show some significant variations. The two independent exocyclic angles (Table 1) at atom C2 differ by some 16°, while those at atom C3 differ by more than 10°. The sense of these deviations suggests strongly repulsive interactions between the methyl group on C2 and the methoxycarbonyl group, although there is a moderate intramolecular C—H···O hydrogen bond between them (Table 3). By contrast, the deviations of the angles (Table 4) at atoms C2 and C3 in (II) become larger, where there is no intramolecular interaction between methyl and acetyl groups. The sums of the three angles around atoms C2 and C3 in (I) are 360.00 (2) and 359.95 (2)°, respectively, and the corresponding values in (II) are 359.99 (2) and 359.92 (2)°, respectively.

It was found that the ^{1}H NMR spectrum of compound (II) shows the methylene H atoms of the pyrrolinone ring as a doublet at δ = 3.34 p.p.m., with an identical coupling constant (J = 2 Hz) to the C2—CH_3 H atoms. The feature is, however, inconsistent with that in (I), where the methylene H atoms give a quartet with coupling constant J = 2.4 Hz. This suggests that, even in solution, the methyl group bonded to C2 in (II) has a stable conformation with respect to the pyrrolinone ring.

In compound (I), the molecules are linked into zigzag chains by a single N—H···O hydrogen bond (Table 2).

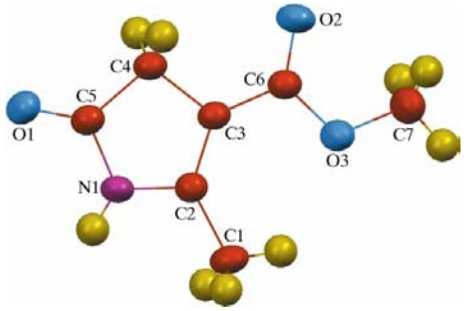


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

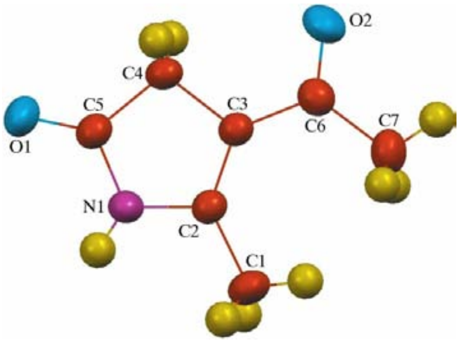


Figure 2
The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

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Heterocyclic atom N1 in the molecule at (x, y, z) acts as a hydrogen-bond donor to carbonyl atom O1 in the molecule at ($2 - x$, $y - \frac{1}{2}$, $\frac{5}{2} - z$), thus forming a $C(4)$ chain (Bernstein *et al.*, 1995) running along the (1, y, $\frac{5}{4}$) direction and generated by a 2_1 screw axis along (1, y, $\frac{5}{4}$) (Fig. 3). Four chains of this type pass through each unit cell; two of these chains, running along the directions (1, y, $\frac{1}{4}$) and (0, y, $\frac{1}{4}$), are related to one another by translational symmetry operations and are antiparallel to the other two chains, running along the (1, y, $\frac{3}{4}$) and (0, y, $-\frac{1}{4}$) directions. There are no direction-specific interactions between adjacent chains.

In a similar way, the supramolecular structure of compound (II) takes on a simple chain packing. For the sake of simplicity, we shall omit any consideration of the intermolecular C—H···O interactions involving a C—H bond from a methyl group, which are unlikely to have any structural significance. The molecules of (II) are connected into infinite chains by a single N—H···O hydrogen bond (Table 4). Heterocyclic atom N1 in the molecule at (x, y, z) acts as a hydrogen-bond donor to carbonyl atom O1 in the molecule at ($-x$, $y - \frac{1}{2}$, $\frac{3}{2} - z$), so generating a $C(4)$ chain running along the (0, y, $\frac{3}{4}$) direction and generated by a 2_1 screw axis along (0, y, $\frac{3}{4}$) (Fig. 4). Four such chains pass through each unit cell; two of these chains, running along the directions (0, y, $\frac{3}{4}$) and (1, y, $\frac{1}{4}$), are related to one another by inversion and are hence antiparallel. There are no direction-specific interactions between adjacent chains.

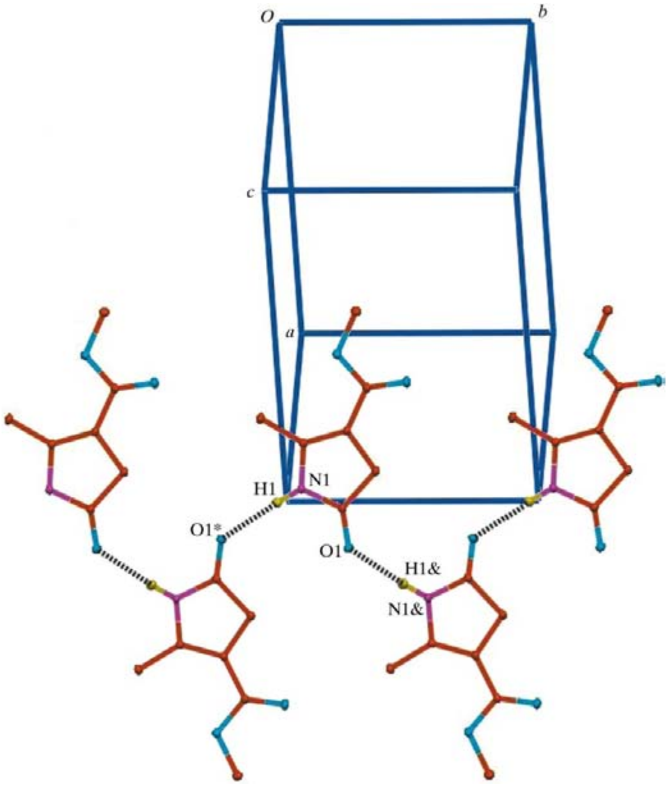

Figure 3
Part of the crystal structure of (I), showing the formation of a $C(4)$ chain running along the (1, y, $\frac{5}{4}$) direction. Atoms marked with an asterisk (*) or an ampersand (&) are at the symmetry positions ($2 - x$, $y - \frac{1}{2}$, $\frac{5}{2} - z$) and ($2 - x$, $\frac{1}{2} + y$, $\frac{5}{2} - z$), respectively.

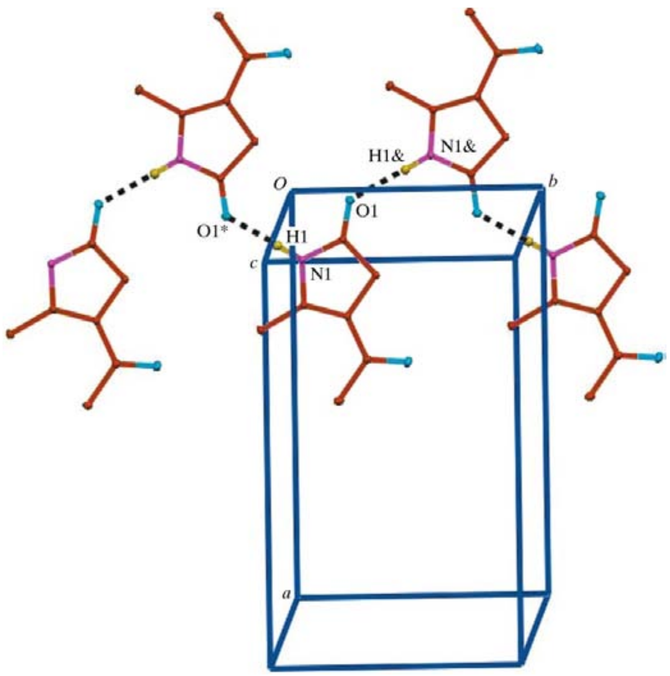

Figure 4
Part of the crystal structure of (II), showing the formation of a $C(4)$ chain running along the (0, y, $\frac{3}{4}$) direction. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or an ampersand (&) are at the symmetry positions ($-x$, $y - \frac{1}{2}$, $\frac{3}{2} - z$) and ($-x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$), respectively.

Experimental

Rather than the published method of San Feliciano *et al.* (1989), a modification of the synthetic procedure was used to prepare (I) and (II). For the synthesis of (I), methyl β-aminocrotonate (23 g) and excess glyoxal (40% in water, 25 ml) were mixed at room temperature in water (80 ml). The mixture was then allowed to stand overnight to give red crystals of (I) (yield 26%). The product was recrystallized from ethyl acetate. ^{1}H NMR ($CDCl_3$): δ 7.76 (*s*, 1H, NH), 3.71 (*s*, 3H, $COOCH_3$), 3.28 (*q*, $J = 2.4$ Hz, 2H, CH_2), 2.35 (*t*, $J = 2.4$ Hz, 3H, CH_3). For the synthesis of (II), excess aqueous ammonia (17%, 0.22 mol) was introduced into a stirred solution of 2,4-pentanedione (20 g, 0.2 mol) in water (80 ml) at room temperature. After 2 h, excess glyoxal (40% in water, 25 ml) was added with stirring and the mixture was allowed to stand overnight to give red crystals of (II) (yield 23%). The product was recrystallized from ethyl acetate. ^{1}H NMR ($CDCl_3$): δ 7.28 (*s*, 1H, NH), 3.34 (*d*, $J = 2$ Hz, 2H, CH_2), 2.38 (*t*, $J = 2$ Hz, 3H, CH_3), 2.20 (*s*, 3H, $COCH_3$).

Compound (I)

Crystal data

$C_7H_9NO_3$
$M_r = 155.15$
Monoclinic, $P2_1/c$
$a = 12.377$ (3) Å
$b = 7.562$ (2) Å
$c = 7.880$ (2) Å
$\beta = 91.509$ (3)°

$V = 737.4$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 291$ (2) K
0.36 × 0.32 × 0.23 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.958$, $T_{\max} = 0.975$

5325 measured reflections
1371 independent reflections
1095 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.142$
$S = 1.31$
1371 reflections
102 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Table 1
Selected bond and torsion angles (°) for (I).

C5—N1—C2	112.74 (14)	C3—C4—C5	103.09 (14)
C3—C2—C1	133.14 (17)	O1—C5—N1	124.57 (16)
N1—C2—C1	117.68 (15)	O1—C5—C4	129.27 (15)
C2—C3—C6	130.69 (16)	N1—C5—C4	106.16 (14)
C6—C3—C4	120.47 (15)		
C5—N1—C2—C3	1.4 (2)	C3—C4—C5—O1	−177.99 (18)
C5—N1—C2—C1	−178.83 (15)	C7—O3—C6—O2	−0.9 (2)
N1—C2—C3—C6	−177.45 (15)	C2—C3—C6—O2	176.11 (17)
N1—C2—C3—C4	−0.10 (19)	C4—C3—C6—O2	−1.0 (2)
C2—C3—C4—C5	−1.00 (16)	C4—C3—C6—O3	179.34 (14)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.86	1.99	2.832 (2)	168

Symmetry code: (i) $-x+2, y-\frac{1}{2}, -z+\frac{5}{2}$.

Compound (II)

Crystal data

$C_7H_9NO_2$
$M_r = 139.15$
Monoclinic, $P2_1/c$
$a = 12.1211$ (18) Å
$b = 7.5078$ (11) Å
$c = 7.9542$ (12) Å
$\beta = 106.740$ (2)°
$V = 693.18$ (18) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 291$ (2) K
0.47 × 0.29 × 0.24 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.954$, $T_{\max} = 0.977$
4420 measured reflections
1289 independent reflections
1150 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.013$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.124$
$S = 1.08$
1289 reflections
94 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}

H atoms were placed in idealized positions and allowed to ride on their respective parent atoms, with C—H = 0.98 Å and N—H = 0.86 Å, and with $U_{\rm iso}({\rm H}) = kU_{\rm eq}$(carrier atom), where $k = 1.2$ for C—H and N—H groups, and 1.5 for methyl groups.

Table 3
Selected geometric parameters (Å, °) for (II).

O1—C5	1.2255 (18)		
C5—N1—C2	112.43 (12)	C6—C3—C4	120.68 (13)
C3—C2—C1	134.51 (14)	C3—C4—C5	103.21 (12)
N1—C2—C1	116.02 (13)	O1—C5—N1	124.12 (14)
C2—C3—C6	130.91 (14)	O1—C5—C4	129.35 (14)
C5—N1—C2—C3	−1.20 (18)	C2—C3—C4—C5	0.82 (15)
C5—N1—C2—C1	178.13 (13)	C3—C4—C5—O1	177.87 (16)
N1—C2—C3—C6	176.86 (14)	C3—C4—C5—N1	−1.49 (15)
N1—C2—C3—C4	0.13 (16)	C2—C3—C6—O2	−174.52 (17)
C1—C2—C3—C4	−179.03 (17)	C4—C3—C6—C7	−179.34 (13)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.86	1.98	2.819 (2)	166

Symmetry code: (i) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$.

For both compounds, data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3127). Services for accessing these data are described at the back of the journal.

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