

3-(1-Hydroxyethylidene)-1-phenyl-
pyrrolidine-2,4-dione

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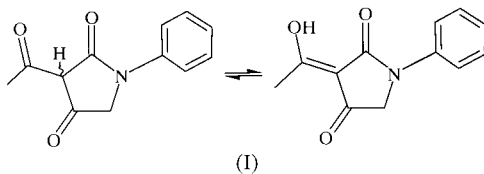
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Analysis of $C_{12}H_{11}NO_3$ revealed a coplanar *N*-substituted phenyl group on a pyrrolidine ring with two keto moieties and a hydroxyethylidene functionality. The hydroxy group forms part of a hydrogen-bonding network characterized by a short intramolecular $H\cdots O$ distance of 1.81 (3) Å, and a longer intermolecular interaction with an $H\cdots O$ distance of 2.38 (3) Å. Both keto groups form additional intra- and intermolecular $C-H\cdots O$ contacts with $H\cdots O$ distances ranging from 2.26 to 2.41 Å.

Comment

The pyrrolidine skeleton occurs in many families of biologically important compounds. The resulting functionality, due to ease of substitution and therefore modification at several positions (Baldwin *et al.*, 1994*a,b*), has been utilized to synthesize compounds with varying properties. For example, several unusual amino acids which contain the pyrrolidine motif were investigated (Galeazzi *et al.*, 1999) and optically active pyrrolidines have been used as intermediates in controlled asymmetric synthesis (Suzuki *et al.*, 1994).



The analysis of crystals grown from a solution of *N*-phenyl-3-acetylpyrrolidine-2,4-dione showed that we had obtained crystals of the related tautomeric form 3-(1-hydroxyethylidene)-1-phenylpyrrolidine-2,4-dione, (I). The title compound (Fig. 1) shows a coplanar pyrrolidine ring with an *N*-substituted phenyl group [dihedral angle between the rings of 0.6 (1)°], substitution at two positions with keto groups and at a third with a hydroxyethylidene moiety. The pyrrolidine atoms do not deviate significantly from their least-squares plane, nor do any of the other non-H atoms [mean deviation, using unit weights, of all non-H atom is 0.02 (3) Å (PLATON; Spek, 2000)].

The bond distances around the N1 atom have a wide range (Table 1) and depend on the nature of the carbon. The shortest distance involves an $N-C_{sp^2}$ bond, followed by an $N-C_{ar}$ of intermediate length with the longest belonging to an $N-C_{sp^3}$ interaction. This results in an asymmetric planar geometry around the nitrogen. The bond geometries correlate well with a variety of *N*-phenyl-substituted pyrrolidin-2-one systems (for example, see Billing *et al.*, 1991).

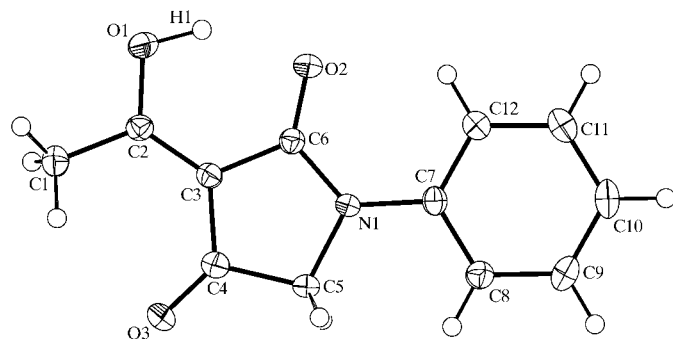


Figure 1

PLATON/ORTEP representation (Spek, 2000) of (I) with displacement ellipsoids at the 50% probability level.

The nature of the hydroxyethylidene side group is confirmed by the $C2=C3$ distance of 1.368 (2) Å, the $C2-O1$ distance of 1.3258 (19) Å, and refinement of H1. The $C-C$ bonds connecting the carbonyl groups show partial double-bond characteristics but are within the range of related bond types observed which have adjoining amino and carbon environments (Allen *et al.*, 1987). The two keto groups also have differing surroundings; thus, $O2=C6$ is involved in a cyclic amino linkage and is slightly longer than $O3=C4$ which has only adjacent C atoms. The geometric parameters concerning both keto functionalities agree with the tabulated compilation.

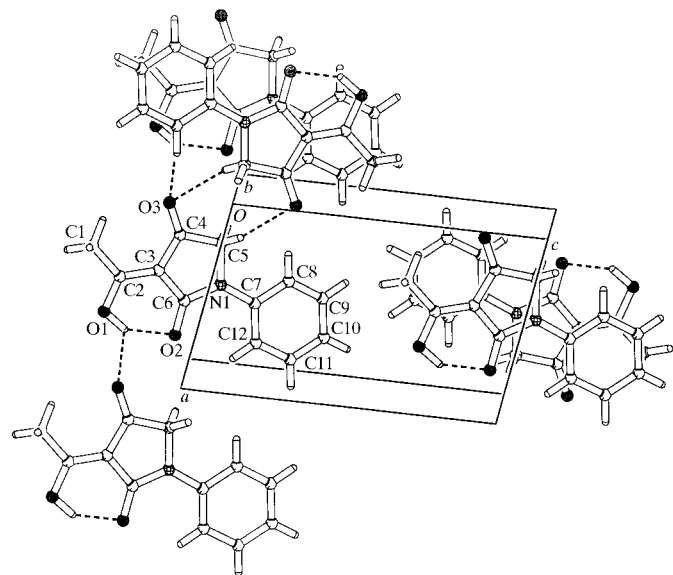


Figure 2

PLATON/PLUTON plot (Spek, 2000) showing part of the hydrogen-bond network and the stacking of molecules.

The hydroxyl group forms an intramolecular contact with O2 and an intermolecular contact to the second keto group O3; H1...O distances of 1.81 (3) Å to O2 and 2.38 (3) Å to O3ⁱ [symmetry code: (i) 1 + x, y, z]. The O1—H1 distance is slightly elongated at 0.99 (2) Å, presumably due to the three-centre (bifurcated) hydrogen-bonding interaction. The geometries are similar to those observed in 2-(1-hydroxyethylidene)indan-1-one (Garcia *et al.*, 1993) and α -cyclopiiazonic acid (van Rooyen, 1992). The molecules form chains along the [100] direction in the crystal and pack in a head-to-tail fashion, due to partial π - π stacking of the hydroxyethylidene group over the phenyl ring. The hydrogen-bonding network is supplemented by weak C—H...O intermolecular contacts between neighbouring molecules (Fig. 2) and extended by C—H...O intramolecular contacts in the plane of the molecule (Table 2).

Experimental

N-Phenyl-3-acetylpyrrolidine-2,4-dione (available from Interbio-screen Ltd) was prepared in a solution of chloroform and ethanol. Colourless crystals of the 'enol' form 3-(1-hydroxyethylidene)-1-phenylpyrrolidine-2,4-dione were obtained by recrystallization from a mixture of chloroform, dichloromethane, methanol and petroleum ether.

Crystal data

C ₁₂ H ₁₁ NO ₃	Z = 2
M _r = 217.22	D _x = 1.449 Mg m ⁻³
Triclinic, P $\bar{1}$	Mo K α radiation
a = 6.5984 (5) Å	Cell parameters from 25 reflections
b = 7.1839 (4) Å	θ = 8.65–15.35°
c = 11.2817 (6) Å	μ = 0.105 mm ⁻¹
α = 103.084 (4)°	T = 150 (2) K
β = 98.380 (5)°	Plate, colourless
γ = 102.485 (5)°	0.50 × 0.50 × 0.08 mm
V = 497.81 (5) Å ³	

Data collection

Nonius CAD-4 diffractometer	h = -8 → 8
ω scans	k = -9 → 9
4924 measured reflections	l = -14 → 14
2279 independent reflections	3 standard reflections
1652 reflections with I > 2 σ (I)	frequency: 60 min
R _{int} = 0.068	intensity decay: <1%
θ_{\max} = 27.47°	

Refinement

Refinement on F ²	w = 1/[$\sigma^2(F_o^2) + (0.0494P)^2 + 0.0415P$]
R[F ² > 2 σ (F ²)] = 0.044	where P = (F _o ² + 2F _c ²)/3
wR(F ²) = 0.116	(Δ/σ) _{max} = 0.001
S = 1.022	$\Delta\rho_{\max}$ = 0.27 e Å ⁻³
2279 reflections	$\Delta\rho_{\min}$ = -0.22 e Å ⁻³
150 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Aromatic H atoms were constrained and allowed to ride on their C atoms with U_{iso}(H) = 1.2U_{eq}(C). The methyl H atoms were constrained to an ideal geometry with U_{iso}(H) = 1.5U_{eq}(C), and allowed to rotate freely about their C—C bonds. The hydroxyl H1 atom was located in the Fourier map and the displacement parameter was freely refined.

Table 1

Selected geometric parameters (Å, °).

N1—C5	1.4732 (18)	O3—C4	1.2205 (19)
N1—C6	1.375 (2)	C2—C3	1.368 (2)
N1—C7	1.412 (2)	C3—C4	1.444 (2)
O1—C2	1.3258 (19)	C3—C6	1.456 (2)
O2—C6	1.2398 (18)		
C6—N1—C7	128.11 (13)	C7—N1—C5	120.66 (12)
C6—N1—C5	111.22 (13)		

Table 2

Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...O2	0.99 (3)	1.81 (3)	2.6948 (18)	147 (2)
O1—H1...O3 ⁱ	0.99 (3)	2.38 (3)	2.8155 (18)	106 (2)
C5—H5B...O3 ⁱⁱ	0.99	2.41	3.328 (2)	154
C1—H1B...O3	0.98	2.38	3.043 (2)	124
C12—H12...O2	0.95	2.26	2.898 (2)	124

Symmetry codes: (i) 1 + x, y, z; (ii) -x, -y, -z.

Data collection: locally modified *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1499). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Baldwin, J. E., Mackenzie Turner, S. C. & Moloney, M. G. (1994a). *Tetrahedron*, pp. 9411–9424.
- Baldwin, J. E., Mackenzie Turner, S. C. & Moloney, M. G. (1994b). *Tetrahedron*, pp. 9425–9438.
- Billing, D. G., Boeyens, J. C. A., Levendis, D. C. & Michael, J. P. (1991). *S. Afr. J. Chem.* **44**, 75–79.
- Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* **A40**, C-410.
- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Galeazzi, R., Geremia, S., Mobbili, G. & Orena, M. (1999). *Tetrahedron Asymmetry*, **10**, 587–605.
- Garcia, J. G., Enas, J. D. & Fronczek, F. R. (1993). *Acta Cryst.* **C49**, 1823–1824.
- Rooyen, P. H. van (1992). *Acta Cryst.* **C48**, 551–552.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (1997). *HELENA*. Utrecht University, The Netherlands.
- Spek, A. L. (2000). *PLATON*. Utrecht University, The Netherlands.
- Suzuki, H., Aoyagi, S. & Kibayashi, C. (1994). *Tetrahedron Lett.* **35**, 6119–6122.