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Self-assembly of 4,6-dipiperidino-1,3,5-triazin-2(1*H*)-one

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The molecules in the crystal structure of the title compound, $C_{13}H_{21}N_5O$, are linked into centrosymmetric dimers through N—H···O=C hydrogen bonds. The piperidine substituents adopt a slightly distorted chair conformation, with an almost planar environment of the N atoms.

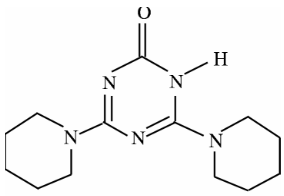
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.081
wR factor = 0.218
Data-to-parameter ratio = 12.1

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

Comment

As part of a study on the self-assembly of triazine derivatives *via* multiple hydrogen-bonding systems (Díaz-Ortiz *et al.*, 2004), the title compound, (I) was prepared by hydrolysis of the corresponding trispiperidine derivative (Elguero *et al.*, 2003).



(I)

The derivatives of 2,3-dihydro-1,3,5-triazine-2-ones may exist in either 2-keto-amine or 2-enol-imine form. In order to determine which of the tautomers is present in the solid state, as well as to establish its supramolecular structure, an X-ray diffraction study of the title compound was undertaken. A search for the 2-keto-amine- and 2-enol-imine-1,3,5-triazine derivatives in the Cambridge Structural Database (CSD;

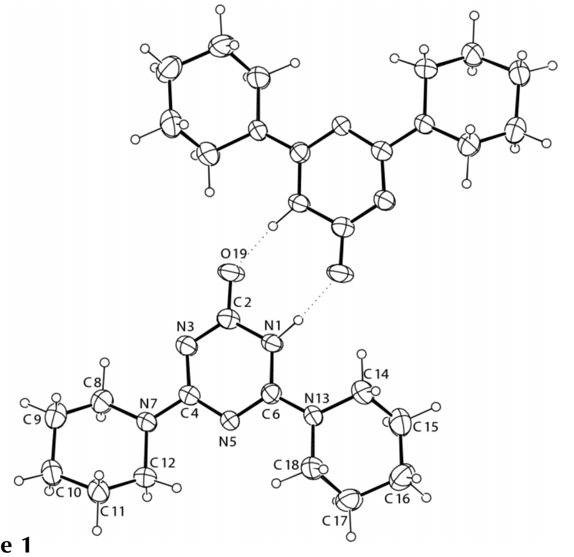


Figure 1
Dimeric aggregates in (I), showing the numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Dotted lines represent hydrogen-bonding interactions.

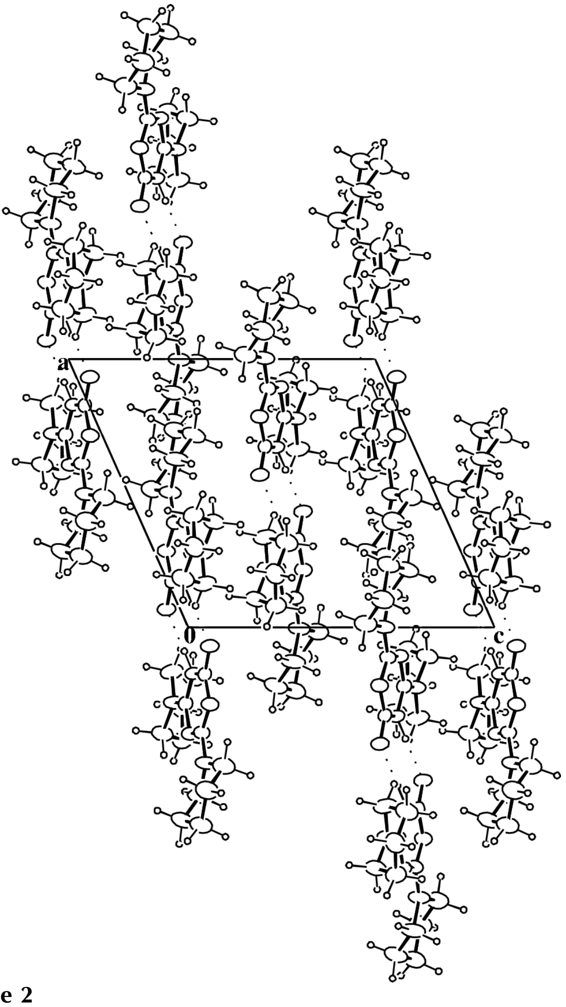
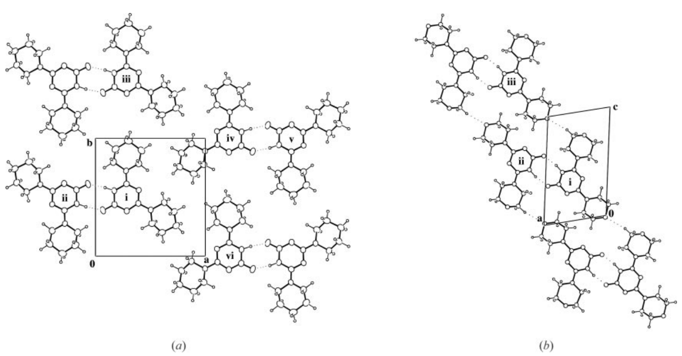


Figure 2
The crystal packing of (I), viewed along the *b* axis, showing the layered structure.

November 2003 release; Allen, 2002) shows that these structures are, in general, quite uncommon, with just four (CSD refcodes CIZRUI, FAJWIW, IHAYEV and IHAYIZ) and one (YICMIG) organic structures found for each of the tautomers, respectively.

In the solid state, the title compound exists as the keto–amine tautomer, (I), this conclusion being based on the experimental location of atom H1, bonded to atom N1, as well as on the C2═O19, N1—C2 and N1—C6 distances and the C2—N1—C6 and N1—C2—N3 angles in the triazine ring (Fig. 1 and Table 1), which are in agreement with the analogous parameters reported previously for keto structures. The piperidine rings adopt a slightly distorted chair conformation, with an almost planar environment of the N atoms (Table 1). The Cremer & Pople (1975) θ parameter for both rings is 2.4 (6)° (*cf.* the ideal value of 0°).

There are several structural differences between the title compound and the closely related 4,6-bis(*N*-morpholino)-1,3,5-triazine-2(1*H*)-one (CSD refcode IHAYEV; Mikhailichenko *et al.*, 2002). At the molecular level, the morpholine close to the NH group is more twisted than the piperidine ring (Table 1).



(*a*) (*b*)

Figure 3
(*a*) Partial crystal packing of (I), viewed along the *c* axis, illustrating the disposition of the dimers within a layer. [Symmetry codes: (i) x, y, z; (ii) $-x, 1-y, -z$; (iii) $x, 1+y, z$; (iv) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $\frac{3}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$; (vi) $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$.] (*b*) Packing of the dimers in the morpholine derivative (IHAYEV; Mikhailichenko *et al.*, 2002), forming a ladder through C—H···O contacts. [Symmetry codes: (i) x, y, z; (ii) $2-x, 1-y, 1-z$; (iii) $1+x, y, 1+z$.]

In the crystal structure of (I), inversion-related molecules aggregate into dimers (Table 2 and Fig. 1) similar to those observed in all the keto–amine structures. Dimers, lying in corrugated sheets (Figs. 2 and 3*a*), are not involved in any significant hydrogen-bonding interactions. By contrast, in the morpholine derivative (IHAYEV), dimers related by translation along the [101] direction form a molecular ladder (Fig. 3*b*) built from C—H···O (morpholine) bonds [H···O 2.46 Å, C···O 3.446 (6) Å and 158°]. The glide of one dimer with respect to the adjacent one, not observed in the title compound [stacks of dimers related by translation along *b* in Fig. 3(*a*)], permits the C—H···O interactions.

The only reported enol form (CSD refcode YICMIG; Shastin *et al.*, 1995) is observed in a 2:1 dioxane solvate. This enol form seems to be favoured over the keto tautomer by the inclusion of two additional potential acceptors of hydrogen bonds, since the dioxane molecule acts as a bridge between two molecules through O—H···O hydrogen bonds.

Experimental

Yttrium trifluoromethane sulfonate (0.08 g, 0.1 mmol), 1-cyanopiperidine (1.10 g, 10 mmol) and anhydrous piperidine (1 ml, 10 mmol) were heated under argon in a screw-cap sealed reaction vessel in an aluminium block at 473 K for 12 h. The crude product was triturated with diethyl ether (3 × 15 ml) and filtered to give a white solid (0.34 g, 31%). A sample of this solid was crystallized from dichloromethane/hexane. The product did not contain any yttrium, but rather represented the hydrolysed triazine derivative, (I).

Crystal data

$C_{13}H_{21}N_5O$
$M_r = 263.35$
Monoclinic, $P2_1/n$
$a = 11.449$ (2) Å
$b = 11.2395$ (17) Å
$c = 11.918$ (3) Å
$\beta = 114.040$ (16)°
$V = 1400.6$ (5) Å^3
$Z = 4$

$D_x = 1.249$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 32 reflections
$\theta = 2$–45°
$\mu = 0.67$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.40 × 0.23 × 0.17 mm

Data collection

Seifert XRD3000-S four-circle diffractometer
$\omega/2\theta$ scans
2390 measured reflections
2130 independent reflections
1170 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\rm max} = 66.7°$
$h = -13 \rightarrow 12$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 13$
2 standard reflections
frequency: 100 min
intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.081$
$wR(F^2) = 0.218$
$S = 1.05$
2130 reflections
176 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0742P)^2 + 1.7012P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.41$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0018 (5)

Table 1
Selected geometric parameters (Å, °).

N1—C6	1.366 (5)	C2—O19	1.240 (5)
N1—C2	1.394 (6)		
C6—N1—C2	121.1 (4)	C8—N7—C12	114.2 (4)
N3—C2—N1	119.0 (4)	C6—N13—C18	121.1 (4)
C4—N7—C8	122.8 (4)	C6—N13—C14	125.5 (4)
C4—N7—C12	121.9 (4)	C18—N13—C14	113.4 (4)
N3—C4—N7—C8	9.4 (8)	N1—C6—N13—C14	−6.7 (8)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O19$^{\rm ii}$	0.78 (5)	2.04 (5)	2.792 (5)	161 (5)
C14—H142···O19$^{\rm ii}$	0.97	2.38	3.219 (6)	144

Symmetry code: (ii) $-x, 1-y, -z$.

The position of atom H1 of the N1—H1 group was determined from a difference map and its coordinates were refined freely, while the $U_{\rm iso}$(H1) value was restricted to be equal to $1.2U_{\rm eq}$(N1). The remaining H atoms were treated as riding, with C—H = 0.97 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C).

Data collection: *XRD*3000-*S* (Seifert, 1996); cell refinement: *LSUCRE* (Appleman, 1984); data reduction: *Xtal*3.6 (Hall *et al.*, 1999); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *Xtal*3.6; software used to prepare material for publication: *SHELXL*97.

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