

1:1 Hetero-assembly of 2-aminopyrimidine and (+)-camphoric acid

Shyamaprosad Goswami,^a Reshmi Mukherjee,^a Kumares Ghosh,^a Ibrahim Abdul Razak,^b S. Shanmuga Sundara Raj^b and Hoong-Kun Fun^{b*}

^aDepartment of Chemistry, Bengal Engineering College, Botanic Garden, Howrah 711103, India, and ^bX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

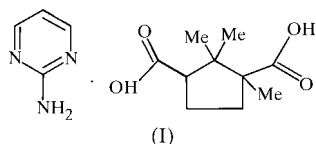
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In the title cocrystal, 2-aminopyrimidine-(+)-camphoric acid (1/1), C₄H₅N₃·C₁₀H₁₆O₄, the 2-aminopyrimidine forms two eight-membered hydrogen-bonded rings with two different camphoric acid molecules. This results in infinite wave-like chains of molecules in which neighbouring chains are connected by weak C—H···O contacts. The five-membered ring in the acid molecule adopts a half-chair conformation.

Comment

Because of their strength as well as directional nature compared with other intermolecular non-covalent interactions (Lehn, 1995), hydrogen bonds are normally used as a tool in designing the structure of molecular crystals. Weak C—H···O contacts play a significant role in determining the molecular packing of organic solids (Taylor & Kennard, 1982). The crystal structure of 2-aminopyrimidine itself has been reported previously (Scheinbeim & Schempp, 1976; Furberg *et al.*, 1979) and both of the pyrimidine-ring N atoms and the amine group form eight-membered rings which leads to hydrogen-bonded self-assembly. The pattern can be changed to a hetero-assembled structure where the donors (acid OH) are paired with the acceptors (ring N) (Etter *et al.*, 1990). This communication reports the structure of the hydrogen-bonded heterodimer of 2-aminopyrimidine with camphoric acid, (I), where the 2-aminopyrimidine is hydrogen-bonded with the camphoric acid moiety to form typical eight-membered rings.



The bond lengths and bond angles of the 2-aminopyrimidine and the camphoric acid molecules are comparable

with the reported values (Etter *et al.*, 1990; Furberg *et al.*, 1979; Barnes *et al.*, 1991). The five-membered ring of the acid molecule adopts a half-chair conformation, as observed in *trans*- π -camphoric acid (Hudson & Mills, 1972), with $\delta C_2(C3) = 0.007(2) \text{ \AA}$ (Nardelli, 1983). The twofold axis passes through C3 and intersects the C1—C5 bond. Atoms C1 and C5 deviate from the mean plane defined by the atoms C2, C3 and C4 by 0.316(5) and $-0.376(5) \text{ \AA}$, respectively.

In the crystal (Fig. 1), each acid molecule is linked to two 2-aminopyrimidine molecules and *vice versa* by N—H···O and O—H···N intermolecular hydrogen bonds to form two symmetry-independent eight-membered rings each of which has the graph-set motif of $R_2^2(8)$ (Bernstein *et al.*, 1995). The eight-membered ring formed between the two moieties belonging to the same asymmetric unit (*i.e.* that ring involving N2 and O2) is almost planar with a maximum deviation from the plane of 0.111(4) \AA for O1. The second eight-membered ring, which contains O4 and N1ⁱ [symmetry code: (i) $\frac{3}{2} - x, 1 - y, z - \frac{1}{2}$], is more twisted with the angle between the two four-atom planes defined by the acid and amine moieties being

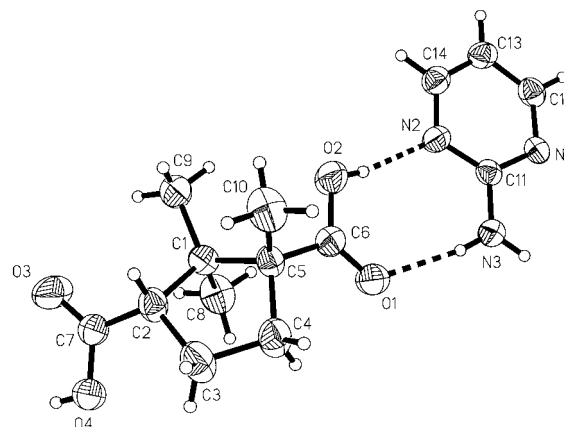


Figure 1

The structure of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme.

$23.8(4)^\circ$. The maximum deviation from the mean ring plane is $0.321(5) \text{ \AA}$ for O3. The mean plane through the five-membered ring in the acid molecule makes dihedral angles of $33.9(2)^\circ$ and $38.3(2)^\circ$, respectively, with the two adjacent pyrimidine rings described above. These hydrogen bonds thereby link the acid and amine moieties into infinite wave-like chains which extend parallel to the *c* axis (Fig. 2). The crystal structure is also characterized by alternate layers of camphoric acid and 2-aminopyrimidine molecules which lie parallel to the *ab* plane. This pattern has also been reported by De Santis *et al.* (1997). The neighbouring chains are interconnected by weak C—H···O interactions (Table 1) and are stacked along the *b* axis with C—H··· π interactions involving the 2-aminopyrimidine molecules of 3.602 \AA [$C13-H13A = 0.93$, $H13A-Cg(-\frac{1}{2} + x, \frac{3}{2} - y, 1 - z) = 2.893 \text{ \AA}$ and $C13-H13A \cdots Cg(-\frac{1}{2} + x, \frac{3}{2} - y, 1 - z) = 134^\circ$ ($Cg = \text{centroid of pyrimidine ring}$)].

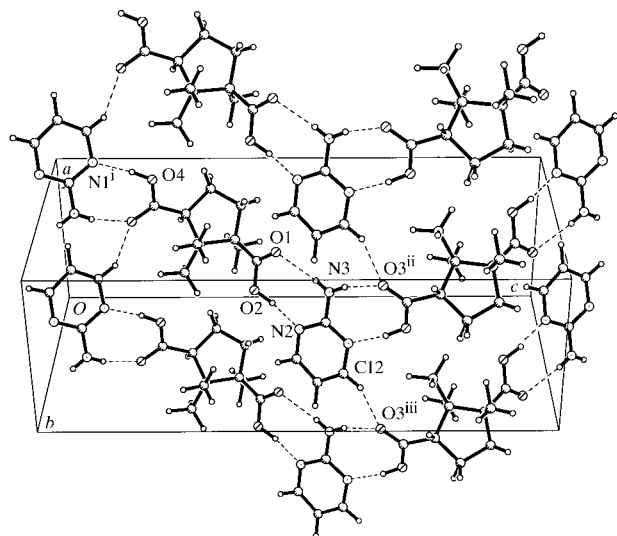


Figure 2
The C—H···O interactions connecting neighbouring chains. The symmetry operators are given in Table 1.

Experimental

Single crystals of (I) were grown by evaporation of a 1:1 mixture of 2-aminopyrimidine and (1*R*,3*S*)-(+)-camphoric acid in ethanol.

Crystal data

$C_4H_5N_3 \cdot C_{10}H_{16}O_4$

$M_r = 295.34$

Orthorhombic, $P2_12_12_1$

$a = 7.146$ (1) Å

$b = 10.561$ (1) Å

$c = 21.306$ (1) Å

$V = 1607.9$ (3) Å³

$Z = 4$

$D_x = 1.220$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 2297 reflections

$\theta = 1.91$ – 28.33°

$\mu = 0.090$ mm⁻¹

$T = 293$ (2) K

Needle, colourless

$0.36 \times 0.16 \times 0.12$ mm

Data collection

Siemens SMART CCD area-detector diffractometer

ω scans

8732 measured reflections

2837 independent reflections

1522 reflections with $I > 2\sigma(I)$

$R_{int} = 0.066$

$\theta_{max} = 25.01^\circ$

$h = -7 \rightarrow 8$

$k = -12 \rightarrow 12$

$l = -23 \rightarrow 25$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.065$

$wR(F^2) = 0.159$

$S = 1.05$

2837 reflections

190 parameters

H atoms constrained

$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.2628P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.15$ e Å⁻³

$\Delta\rho_{min} = -0.15$ e Å⁻³

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2—H2B···N2	0.82	1.87	2.665 (5)	163
O4—H4C···N1 ⁱ	0.82	1.90	2.713 (4)	170
N3—H3D···O1	0.86	2.06	2.910 (5)	170
N3—H3C···O3 ⁱⁱ	0.86	2.13	2.951 (5)	161
C12—H12A···O3 ⁱⁱⁱ	0.93	2.59	3.221 (6)	125

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

After checking their presence in the difference map, the positions of all H atoms were geometrically idealized and allowed to ride on their parent atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1090). Services for accessing these data are described at the back of the journal.

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