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2-Aminopyrimidine and *p*-phenylenediacetic acid (1:1) co-crystal

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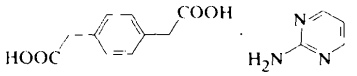
Abstract

In the title co-crystal, each 2-aminopyrimidine molecule, $C_4H_5N_3$, participates in two eight-membered hydrogen-bonded rings with carboxylic acid groups from two different phenylenediacetic acid molecules, $C_{10}H_{10}O_4$. This results in infinite hydrogen-bonded chains. In the supramolecular structure, the chains are held together by weak C—H···O contacts.

Comment

Hydrogen bonds are used extensively as a tool to design the structure of molecular crystals, because of their strength, as well as their directional nature, compared to other intermolecular non-covalent interactions (Lehn, 1995). Most of the supramolecular crystals originate from strong N—H···*X* and O—H···*X* (*X* = O, N) hydrogen bonds. Weak C—H···O bonds are known to play a significant role in determining the molecular packing of organic solids (Taylor & Kennard, 1982). 2-Aminopyrimidine forms heterodimeric structures with different mono- and dicarboxylic acids (Etter & Adsmond, 1990; Etter *et al.*, 1990), rather than their individual self assembly (Scheinbeim *et al.*, 1976). We have also recently shown (Goswami *et al.*, 1999) that terephthalic acid forms chain-like heteroassemblies with 2-aminopyrimidine, similar to those formed by 2-aminopyrimidine and succinic acid (Etter *et al.*, 1990). In this paper, we report the supramolecular structure of the 2-aminopyrimidine–*p*-phenylenediacetic acid co-crystal, (I), *via* C—H···O hydrogen bonding.



(I)

The asymmetric unit consists of one half-molecule each of 2-aminopyrimidine and *p*-phenylenediacetic acid; the 2-aminopyrimidine lies on a crystallographic twofold axis passing through atoms N2, C6 and C8, and the *p*-phenylenediacetic acid is on an inversion centre.

Bond lengths and angles in the 2-aminopyrimidine agree with other reported values (Byriel *et al.*, 1992; Lynch *et al.*, 1994). The carboxylic acid group (O1, O2, C4 and C5) makes dihedral angles of 77.6 (1) and 2.5 (1)° with the planes of the phenyl ring and the 2-aminopyrimidine moiety, respectively. The planar 2-aminopyrimidine is linked to the *p*-phenylenediacetic acid by N2—H1N2···O1 and O2—H1O2···N1 intermolecular hydrogen bonds; along with C5 and C6, they form an eight-membered ring, which is coplanar with the pyrimidine moiety. Since both molecules lie across crystallographic symmetry elements, the hydrogen-bond system is extended to form an infinite chain-like structure in the solid state. Neighbouring chains along the *a* axis are linked by weak C4—H4*B*···O1^{i} contacts to form a supramolecular assembly (Fig. 2), in which the pyrimidine and phenyl rings are stacked with perpendicular separations of 3.605 (4) and 3.614 (4) Å, respectively [symmetry code: (i) $x - 1, y, z$].

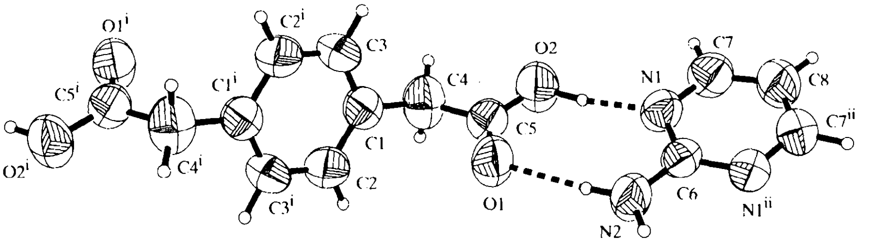


Fig. 1. The structure of the title co-crystal, showing 50% probability displacement ellipsoids and the atom-numbering scheme [symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $1 - x, y, \frac{3}{2} - z$].

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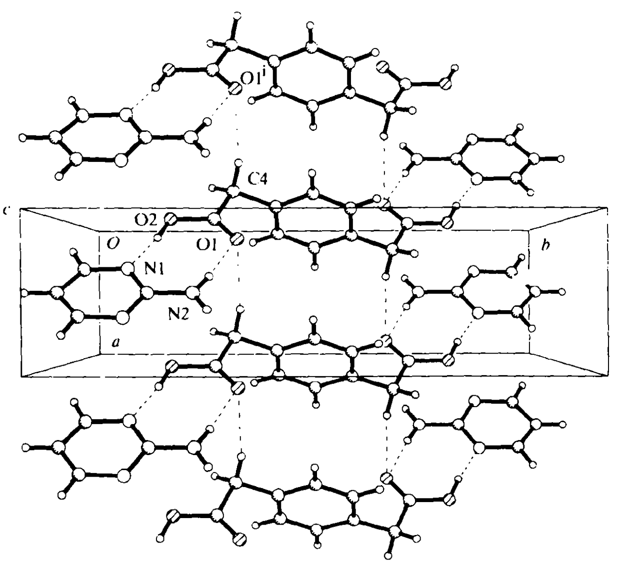

Fig. 2. A view of the supramolecular structure of (I) [symmetry code: (i) $x - 1, y, z$].

Experimental

Single crystals of (I) were grown by slow evaporation of a dry acetone solution of 2-aminopyrimidine and *p*-phenylenediacetic acid (1:1 molar ratio).

Crystal data

$C_4H_5N_3 \cdot C_{10}H_{10}O_4$
$M_r = 289.29$
Orthorhombic
Pbcn
$a = 4.5686 (1)$ Å
$b = 15.7687 (2)$ Å
$c = 20.1621 (4)$ Å
$V = 1452.50 (5)$ Å^3
$Z = 4$
$D_x = 1.323$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 3724 reflections
$\theta = 2.77$–$33.18°$
$\mu = 0.099$ mm^{-1}
$T = 293 (2)$ K
Block
0.58 × 0.44 × 0.38 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
11 260 measured reflections
2515 independent reflections

1286 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\rm max} = 32°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 23$
$l = 0 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.161$
$S = 1.084$
2515 reflections
128 parameters
All H-atom parameters refined

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.119$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.096$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.026 (3)

$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.2796P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.1400 (3)	0.35048 (8)	0.64565 (7)	0.0956 (5)
O2	0.0011 (4)	0.22373 (9)	0.61149 (8)	0.0961 (5)
N1	0.3388 (4)	0.15077 (9)	0.70366 (7)	0.0756 (5)
N2	1/2	0.27532 (15)	3/4	0.0903 (8)
C1	−0.0970 (4)	0.42296 (11)	0.52668 (9)	0.0692 (5)
C2	−0.1812 (5)	0.49945 (14)	0.55305 (11)	0.0881 (6)
C3	0.0850 (5)	0.42488 (13)	0.47323 (10)	0.0867 (6)
C4	−0.1966 (6)	0.33973 (16)	0.55521 (14)	0.0929 (7)
C5	−0.0014 (4)	0.30613 (12)	0.60887 (9)	0.0718 (5)
C6	1/2	0.19082 (16)	3/4	0.0680 (6)
C7	0.3460 (5)	0.06616 (13)	0.70459 (10)	0.0864 (6)
C8	1/2	0.0207 (2)	3/4	0.0928 (9)

Table 2. *Selected bond lengths (Å)*

O1—C5	1.207 (2)	N1—C6	1.3469 (18)
O2—C5	1.300 (2)	N2—C6	1.333 (3)
N1—C7	1.335 (2)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1O2···N1	1.02 (3)	1.66 (3)	2.675 (2)	171 (2)
N2—H1N2···O1	0.90 (2)	2.02 (2)	2.922 (2)	174 (2)
C4—H4*B*···O1ⁱ	1.00 (3)	2.56 (3)	3.541 (3)	168 (2)

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

The data collection covered a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 10 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm ($2\theta_{\rm max} = 66.36°$) and the detector swing angle was −35°. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the duplicate reflections, and was found to be negligible. Only reflections having 2θ less than 64° were used for structure solution and refinement, as only a few reflections were found to be observed at higher angles. The structure was solved by direct methods and refined by full-matrix least-squares techniques. All H atoms were located from a difference Fourier map and refined isotropically.

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 *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1242). Services for accessing these data are described at the back of the journal.

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2-[3-(Pyrrolidin-1-yl)cyclohex-2-en-1-ylidene]propanedinitrile

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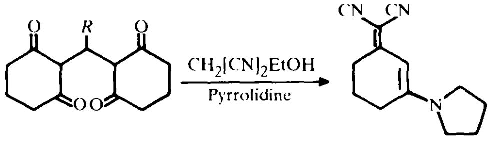
Abstract

In the title compound, $C_{13}H_{15}N_3$, the cyclohexene ring adopts a conformation intermediate between sofa and half-chair, and the substituted pyrrolidine ring assumes a conformation intermediate between envelope and half-chair. The dihedral angle between the pyrrolidine and cyclohexene rings is 7.2 (1)°. The propanedinitrile group occupies the equatorial position with respect to the cyclohexene ring.

Comment

Applications of malononitrile in organic chemistry comprise the synthesis of unique heterocyclic systems, pharmaceuticals, pesticides, fungicides and solvato-chromic dyes (Fatiadi, 1978). The pyrrolidine part of the title compound has useful medicinal properties. Pyrrolidine derivatives inhibit the production of prostaglandin E2 and intracellular phospholipase A2, and are useful for prevention and treatment of rheumatoid arthritis, asthma, allergies, rhinitis and related diseases (Mitsuaki *et al.*, 1997). Some of the aminopyrrolidine products are used as pharmaceutical and agrochemical intermediates (Fumiaki & Shozo, 1997). The pyrrolidine–cyclohexyl compounds act as highly-lipophilic chemically-novel potent selective kappa opioid agonists (Sabin *et al.*, 1997) and were found to be preferential dopamine autoreceptor antagonists (Haekan *et al.*, 1997). Some of the arylpyrrolidine derivatives are used as insecticides, acaricides and herbicides (Santel *et al.*, 1997). In view of the above medicinal significance, the title compound was investigated to define the conformation of the cyclohexene ring with respect to the pyrrolidine ring of the molecule.



(1) $R = H$
(2) $R = CH_3$
(3)

An *ORTEP* drawing (Zsolnai, 1997) of the molecule with atomic numbering scheme is shown in Fig. 1. Cremer & Pople (1975) puckering parameters show that the cyclohexene ring is in a half-chair conformation, distorted towards a half-boat [Q = 0.461 (2) Å, θ = 56.0 (2)° and φ = −111.8 (3)°] (Duax & Norton, 1975; Caracelli *et al.*, 1997). The conformation of the pyrrolidine ring assumes an intermediate between an envelope and a half-chair conformation as seen by the ring puckering parameters [Q = 0.129 (4) Å and φ = 52.1 (1)°] (Zukerman-Schpector *et al.*, 1984). C11 and C12 in the pyrrolidine ring have high anisotropic dis-

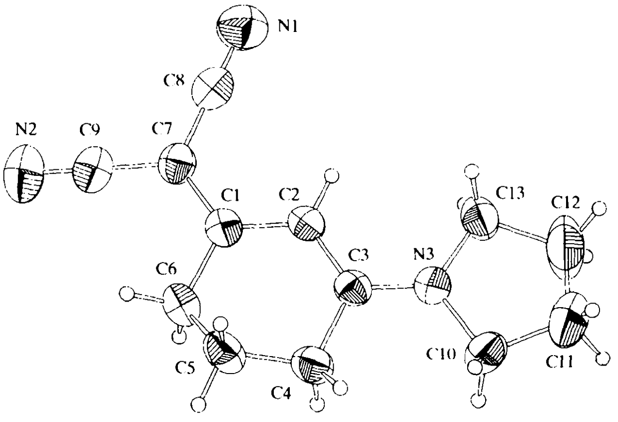


Fig. 1. Molecular structure of the title compound with 50% probability displacement ellipsoids. H atoms have been assigned as circles of an arbitrary radius.