Acta Cryst. (1999). C**55**, 583–585

2-Aminopyrimidine–fumaric acid cocrystal

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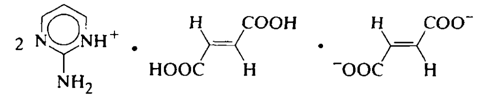
(Received 18 August 1998; accepted 28 October 1998)

Abstract

In crystals of the title compound, 2-aminopyrimidin-1-ium hemifumarate hemifumaric acid, $C_4H_6N_3^+\cdot0.5C_4H_2O_4^{2-}\cdot0.5C_4H_4O_4$, the asymmetric unit contains one 2-aminopyrimidine cation, $C_4H_6N_3^+$, protonated at a pyrimidine ring-N atom, one half-molecule of fumaric acid, $C_4H_4O_4$, and one half of a fumarate ion, $C_4H_2O_4^{2-}$. These are linked by N—H···O, O—H···O and relatively strong C—H···O bonds, resulting in eight- and nine-membered hydrogen-bonded rings and an extended supramolecular structure.

Comment

Supramolecular assembly is a central theme in the design of new solid state structures with unusual conductance, electronic, non-linear optical or magnetic properties (Disalvo, 1990). Such an assembly has been observed in the cocrystal of 2-aminopyrimidine with terephthalic acid (1:1) (Goswami *et al.*, 1999). The crystal structure of 2-aminopyrimidine itself has been reported (Scheinbeim & Schempp, 1976), in which two equivalent proton donors and two equivalent acceptors make an eight-membered hydrogen-bonded self-assembly. This communication reports the crystal structure of 2-aminopyrimidine with fumaric acid, (I), in which 2-aminopyrimidine makes typically eight- and nine-membered hydrogen-bonded rings with fumaric acid. The structure of the complex shows that a strong interaction alone need not always dictate the crystal structure if other weaker interactions are of special significance. This indicates that caution must be taken to keep track of weak interactions while designing novel structures of new materials.



(I)

The asymmetric unit of (I) contains one 2-aminopyrimidine cation, one half-molecule of fumaric acid and one half of a fumarate dianion. The fumarate dianion is formed through the protonation of 2-aminopyrimidine by fumaric acid: this type of protonation is observed in other carboxylic acid and 2-aminopyrimidine cocrystals (Byriel *et al.*, 1992; Lynch *et al.*, 1994).

The bond lengths and angles in the 2-aminopyrimidine agree with the values observed for the protonated molecule (Byriel *et al.*, 1992; Lynch *et al.*, 1994). The geometries of the fumaric acid and fumarate dianion are comparable with those reported by Brown (1966) and Li & Mak (1997). The fumaric acid and its dianion form a dihedral angle of 12.51 (8)°, and they make dihedral angles of 27.66 (9) and 16.74 (9)°, respectively, with the 2-aminopyrimidine.

Within the asymmetric unit, the 2-aminopyrimidine is linked to the fumaric acid and fumarate dianion by N1—H···O3, N2—H···O4, O2—H···O4 and C2—H···O1 hydrogen bonds, through the formation of eight- and nine-membered hydrogen-bonded rings (Table 2 and Fig. 1). These hydrogen bonds, together with N1—H···O1$(x, \frac{3}{2}-y, \frac{1}{2}+z)$ and the crystallographic symmetry elements (the fumarate molecule and anion lie

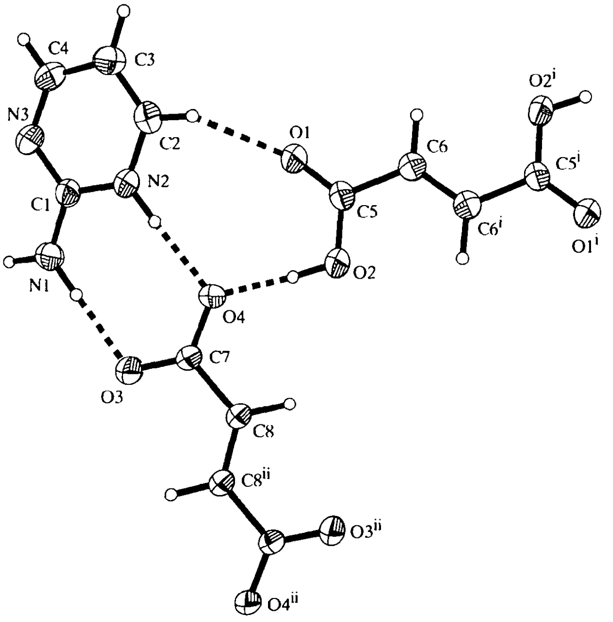


Fig. 1. The structure of title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme. Symmetry codes are as in Table 1.

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on inversion centres), result in extended 'wavy' sheets parallel to the (100) plane. Adjacent sheets are linked by three weaker C—H···O hydrogen bonds to form a supramolecular assembly, which is further stabilized by the interactions between the pyrimidines within their stacks (Fig. 2).

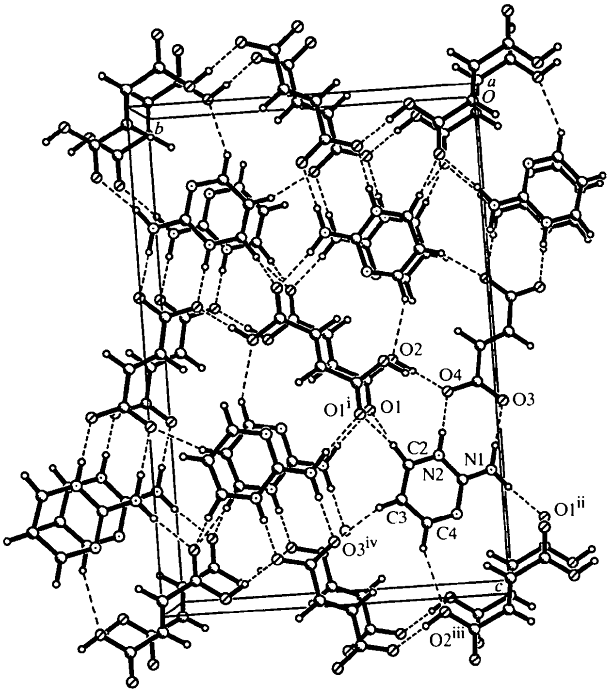

Fig. 2. Packing of the molecules of (I), viewed normal to the (100) plane. Symmetry codes are as in Table 2.

Experimental

Single crystals were grown by slow evaporation of a solution of 2-aminopyrimidine and fumaric acid (1:1 molar ratio) in a 6:1 mixture of dry acetone and methanol.

Crystal data

$C_4H_6N_3^+ \cdot 0.5C_4H_2O_4^{2-} \cdot$
$0.5C_4H_4O_4$
$M_r = 211.18$
Monoclinic
$P2_1/c$
$a = 3.7946\ (2)$ Å
$b = 19.1766\ (7)$ Å
$c = 13.0641\ (6)$ Å
$\beta = 96.893\ (1)°$
$V = 943.77\ (7)$ Å^3
$Z = 4$
$D_x = 1.486$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 3463 reflections
$\theta = 3.14–33.12°$
$\mu = 0.121$ mm^{-1}
$T = 293\ (2)$ K
Slab
$0.48 \times 0.24 \times 0.18$ mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω-scans
Absorption correction: none
7257 measured reflections
2752 independent reflections
1830 reflections with $I > 2\sigma(I)$

$R_{int} = 0.042$
$\theta_{max} = 30°$
$h = -5 \rightarrow 5$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.184$
$S = 1.055$
2752 reflections
172 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0917P)^2 + 0.1819P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.387$ e Å^{-3}
$\Delta\rho_{min} = -0.227$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

O1—C5	1.209 (3)	N3—C1	1.349 (3)
O2—C5	1.306 (3)	C2—C3	1.364 (3)
O3—C7	1.233 (2)	C3—C4	1.394 (3)
O4—C7	1.284 (2)	C5—C6	1.491 (3)
N1—C1	1.322 (3)	C6—C6^{i}	1.310 (4)
N2—C2	1.352 (3)	C7—C8	1.494 (3)
N2—C1	1.355 (3)	C8—C8^{ii}	1.311 (4)
N3—C4	1.324 (3)		

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, 1-y, 2-z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N1···O3	0.96 (3)	1.84 (3)	2.796 (3)	176 (3)
N2—H1N2···O4	0.91 (3)	1.80 (3)	2.708 (2)	170 (3)
O2—H1O2···O4	0.93 (3)	1.63 (3)	2.551 (2)	172 (3)
C2—H2···O1	0.96 (3)	2.48 (3)	3.068 (3)	119 (2)
C2—H2···O1^{i}	0.96 (3)	2.56 (3)	3.378 (3)	143 (2)
N1—H2N1···O1^{ii}	0.95 (3)	1.93 (3)	2.875 (3)	174 (2)
C4—H4···O2^{iii}	0.97 (3)	2.58 (3)	3.440 (3)	149 (2)
C3—H3···O3^{iv}	0.97 (3)	2.43 (3)	3.367 (3)	162 (2)

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

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 30 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm ($2\theta_{max} = 66.24°$) and the detector swing angle was −35°. Coverage of the unique set is over 99% complete. 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 60° were used for structure solution and refinement, as only a few reflections were found to be observed at higher angles. 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 *PARST* (Nardelli, 1995).

SG and AKM are thankful to the CSIR, New Delhi, India, for financial support. The authors would also like to thank the Malaysian Government for research grant R&D No. 190-9609-2801. KC thanks the Universiti Sains Malaysia for a Visiting Post-Doctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1239). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 585-586

5,10-Dimethoxy-1,4-methano-1,4,4a,11a-tetrahydrobenzo[*b*]fluoren-11-one oxime

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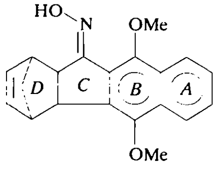
(*Received 27 July 1998; accepted 16 November 1998*)

Abstract

In the title compound, $C_{20}H_{19}NO_3$, the oxime moiety C=N—O—H adopts a *trans* conformation. Furthermore, the molecule as a whole exists in a dimeric form through hydrogen bonding between the oxime groups.

Comment

The title compound was prepared in connection with our work on the synthesis of phenanthroviridin, an anticancer drug (Gore *et al.*, 1992). The X-ray structure determination of the title compound, (I), was undertaken in order to determine the stereochemistry of the oxime moiety, which is very important for the planned Beckmann rearrangement.



(I)

The bond lengths and angles observed in this structure have normal values (Allen *et al.*, 1987; Beddoes *et al.*, 1993); the C9—C10 and N1—C6 bonds show double-bond character. The oxime moiety C=N—O—H adopts a *trans* conformation. The six-membered ring, *D*, of the norbornene ring system is a fairly symmetrical boat with asymmetry parameters ΔC_s(C7—C12) = 0.019 (1) and ΔC_s(C8) = 0.024 (1) (Nardelli, 1983). The two five-membered rings in the norbornene moiety formed by the bridging atom C14 adopt envelope conformations. The angles between the three-atom bridge plane C8—C14—C11 and four-atom planes of the six-membered rings (C8, C9, C10, C11 and C7, C8, C11, C12) are 52.0 (2) and 60.2 (2)°, respectively. The C9—C10—C7—C12 plane is nearly perpendicular [dihedral angle 87.59 (8)°] to the five-membered ring *C*. In the solid state, inversion-related molecules exist in dimeric form through O—H···N hydrogen bonding (Table 2).

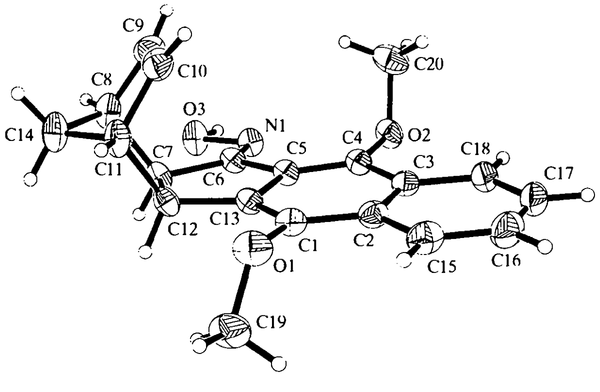


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Experimental

To synthesize the title compound, 3-phenylsulphonylphthalide (1.100 mg, 4.0 mmol) was allowed to react with tricyclo-

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