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Hydrogen-bonded azopyridine and succinic acid co-crystal

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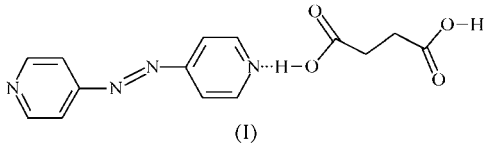
In the 1:1 supramolecular adduct of azopyridine (AZP) and succinic acid (SA) [systematic name: di-4-pyridyldiazene–succinic acid (1/1)], $C_{10}H_8N_4{\cdot}C_4H_6O_4$ or AZP·SA, both components lie on inversion centers. Alternating AZP and SA molecules are linked by O—H···N hydrogen bonds to form a linear chain extending in the $[31\bar{1}]$ direction. Between chains there is a strong pyridyl–azo π–π interaction, with a 3.340 Å separation between the inversion center at the midpoint of the azo bond and the centroid of the pyridine ring; this interaction results in the formation of sheets.

Comment

Crystal engineering allows control of the stacking of molecules and molecular adducts by covalent and especially non-covalent interactions, such as hydrogen-bonding or π–π interactions. This approach is attractive for the design and fabrication of functional materials (Aakeröy & Seddon, 1993; Aoyama *et al.*, 1996; Kuduva *et al.*, 1999, 2001; Muthuraman *et al.*, 2001). Recently, much effort has been made in exploring the crystallization regularity of aza-aromatic molecules with the presence of carboxylic acid as the supramolecular synthons (Bond, 2003; Bhogala & Nangia, 2003; Vishweshwar *et al.*, 2002). The co-crystallization of 4,4′-bipyridyl in the presence of fumaric acid (FA) and adipic acid (AA), and



(I)

the orderliness of 4,4′-bipyridyl and dicarboxylic acids around the aspect of odd and even $-CH_2-$ numbers, have been reported (Pedireddi *et al.*, 1998; Chatterjee *et al.*, 1998). In previous work, we have reported the preparation of a series of co-crystals of aza-aromatic molecules with dicarboxylic acids, *viz*. BPE·SA, AZP·FA, BPE·AA, AZP·AA, AZP·SEA and AZP·OA [BPE is 1,2-bis(4-pyridyl)ethylene, AZP is azopyridine, SA is succinic acid, SEA is sebacic acid and OA is oxalic acid], and revealed the regularity of their supramolecular alignments driven by hydrogen bonding (Zhang *et al.*, 2003, 2002; Wu *et al.*, 2002).

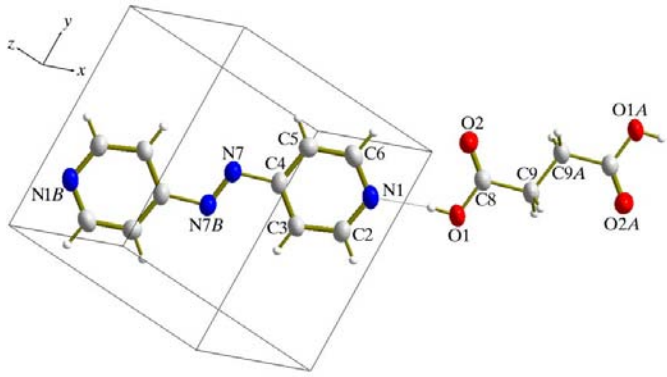


Figure 1
A 50% probability displacement ellipsoid diagram of the AZP·SA adduct. Atoms labeled with the suffixes *A* and *B* are at positions $(4-x, 2-y, -z)$ and $(1-x, 1-y, 1-z)$, respectively.

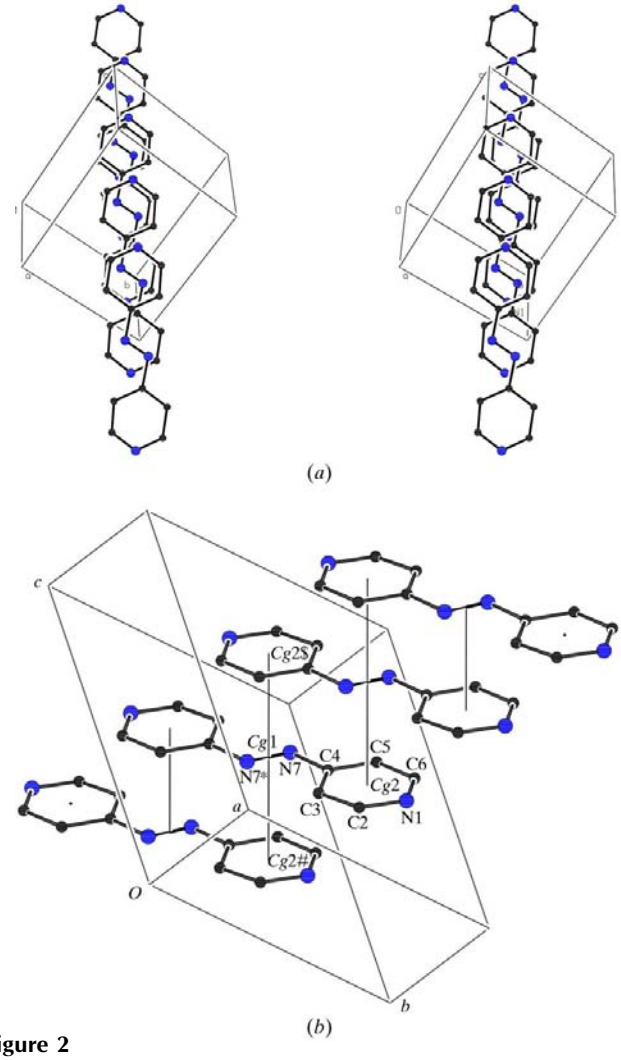


Figure 2
(*a*) A stereoview of the AZP overlap, showing the pyridyl–azo π–π intrasheet interaction. (*b*) A view showing details of the π–π interactions; atoms labeled with an asterisk (*), a dollar sign ($) or a hash (#) are at equivalent positions $(1-x, 1-y, 1-z)$, $(2-x, 1-y, 1-z)$ and $(x-1, y, z)$, respectively.

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As an extension of this previous work, we have prepared a new co-crystal, a 1:1 adduct, *viz*. AZP·SA, (I), of azopyridine and succinic acid, which should exhibit the stacking regularity noted previously (Zhang *et al.*, 2003) and which we wish to compare with the structure of the 1:1 BPE·SA complex, (II).

The AZP and SA components in (I) lie on independent inversion centers, as shown in Fig. 1, and are linked by O—H···N hydrogen bonds between alternating AZP and SA molecules. This configuration results in a linear chain of molecules extending in the [31$\bar{1}$] direction. The dihedral angle between the planes of the O1/O2/C8 SA carboxyl group and the N1/C2–C6 pyridyl ring is 9.2 (3)°. Compound (II) is isostructural with (I) and has an exactly analogous packing; the corresponding dihedral angle is larger [21.3 (3)°]. The two pyridyl rings in (I) are exactly parallel by symmetry but are slightly stepped [0.026 (4) Å]; the corresponding value for (II) is 0.097 (6) Å. The length of the AZP long axis in (I), between atoms N1 and N1*B* [at $(1-x, 1-y, 1-z)$] (Fig. 1), is 9.013 (10) Å; for the SA molecule, the distance between the hydroxy H atom and the equivalent atom at $(4-x, 2-y, -z)$ is 7.27 Å. The corresponding data in (II) [9.407 (4) and 7.29 Å, respectively] show that the BPE molecule is slightly longer than the AZP molecule.

As illustrated in Figs. 2(*a*) and 2(*b*), the hydrogen-bonded chains in (I) are oriented so that there is an overlap between the pyridyl rings and azo groups in adjacent chains, consistent with strong pyridyl–azo π–π intrasheet interactions. The distance between the center (*Cg*1) of the azo group [at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$] and the centroids (*Cg*2\$ and *Cg*2#) of adjacent pyridyl rings [at $(2-x, 1-y, 1-z)$ and $(x-1, y, z)$, respectively] is 3.340 Å.

In (II), as well as π–π interactions, there is a significant C—H···O interchain hydrogen bond between an aromatic CH group and an adjacent hydroxy O atom, with an H···O distance of 2.46 Å, a C···O distance of 3.376 (3) Å and a C—H···O angle of 160°. The small difference (0.394 Å) between the lengths of the AZP and BPE molecules as measured by the pyridyl N···N intramolecular separations in BPE and AZP preclude an exact match of the packing in (I) and (II). In the packing competition to link chains, it is the drive to form sheets of molecules *via* π–π interactions that wins out over the drive to form sheets of molecules linked by C—H···O interactions; the result is a weaker C—H···O contact geometry in (I), with an H···O distance of 2.62 Å (Table 1 and Fig. 3).

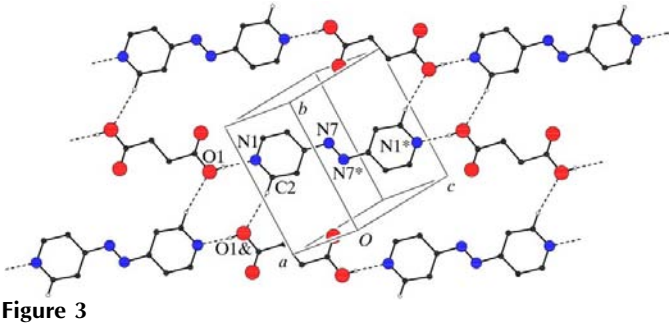

Figure 3
A packing diagram showing the general chain arrangement and the weak C—H···O interactions between chains; atom O1& is at equivalent position $(3-x, 1-y, -z)$ and atoms labeled with an asterisk (*) are at $(1-x, 1-y, 1-z)$.

Experimental

AZP was synthesized following the procedures described by Brown & Granneman (1975). AZP was co-crystallized with SA in a 1:1 molar ratio. In order to obtain high-quality crystals, they were mixed in a solution of acetone and ethanol (2:1 *v*/*v*), warmed until they dissolved completely and allowed to stand at room temperature for several days. After most of the solvent had evaporated, co-crystals of AZP·SA suitable for X-ray analysis were obtained.

Crystal data

$C_{10}H_8N_4·C_4H_6O_4$
M_r = 302.29
Triclinic, $P\bar{1}$
a = 4.738 (4) Å
b = 8.954 (9) Å
c = 9.073 (10) Å
α = 108.33 (4)°
β = 92.84 (4)°
γ = 99.98 (4)°
V = 357.6 (6) Å^3
Z = 1
D_x = 1.404 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2708 reflections
θ = 7.9–54.9°
μ = 0.11 mm^{-1}
T = 298 (2) K
Block, red
0.50 × 0.29 × 0.17 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995).
T_{min} = 0.875, T_{max} = 1.000
3428 measured reflections
1601 independent reflections
1290 reflections with $I > 2\sigma(I)$
R_{int} = 0.011
θ_{max} = 27.5°
$h = -5 \rightarrow 6$
$k = -11 \rightarrow 11$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.138
S = 1.14
1601 reflections
101 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0778P)^2 + 0.0314P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.82	1.85	2.660 (2)	170
C2—H2···O1^{i}	0.93	2.62	3.481 (3)	155

Symmetry code: (i) $3-x, 1-y, -z$.

H atoms were visible in difference maps and were subsequently allowed for as riding, with C—H distances of 0.93 Å for pyridyl H atoms and 0.97 Å for methylene H atoms, an O—H distance of 0.82 Å and U_{iso}(H) values of 1.2U_{eq}(C,O).

Data collection: *R-AXIS RAPID Diffractometer Control Software* (Rigaku, 2001); cell refinement: *SHELXTL* (Bruker, 2000); data reduction: *R-AXIS RAPID Diffractometer Control Software*; program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1785). Services for accessing these data are described at the back of the journal.

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