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2,3-Diaminopyridinium (2*E*,4*E*)-hexa-2,4-dienoate

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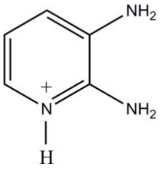
Key indicators: single-crystal X-ray study; *T* = 296 K; mean σ(C–C) = 0.003 Å; *R* factor = 0.049; *wR* factor = 0.111; data-to-parameter ratio = 13.3.

In the title salt, $C_5H_8N_3^+\cdot C_6H_7O_2^-$, the pyridine N atom of the 2,3-diaminopyridine molecule is protonated. The 2,3-diaminopyridinium cation is essentially planar, with a maximum deviation of 0.068 (2) Å for one of the amino N atoms. The sorbate anion adopts an extended conformation. In the crystal structure, the protonated N atom and one of the two amino-group H atoms are hydrogen bonded to the sorbate anion through a pair of N—H···O hydrogen bonds, forming an $R_2^2(8)$ ring motif. The ion pairs are further connected *via* intermolecular N—H···O and C—H···O hydrogen bonds, forming two-dimensional networks parallel to (100).

Related literature

For details of non-covalent interactions, see: Desiraju (1995); Moulton & Zaworotko (2001); Biradha & Fujita (2002). For applications of sorbic acid, see: Martindale (1996); Richards (1972). For related structures, see: Cox (1994); Thanigaimani *et al.* (2007); Raj *et al.* (2003). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For standard bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_5H_8N_3^+\cdot C_6H_7O_2^-$
$M_r = 221.26$
Monoclinic, $P2_1/c$
$a = 9.0440$ (3) Å
$b = 10.6964$ (3) Å
$c = 12.4632$ (4) Å
$\beta = 94.947$ (2)°
$V = 1201.18$ (6) Å^3
$Z = 4$
Mo *K*α radiation
$\mu = 0.09$ mm^{-1}
$T = 296$ K
0.15 × 0.15 × 0.09 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min} = 0.987$, $T_{max} = 0.993$
8260 measured reflections
2736 independent reflections
1794 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.111$
$S = 1.02$
2736 reflections
205 parameters
All H-atom parameters refined
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*1···O2	1.00 (2)	1.66 (2)	2.6591 (19)	174.7 (18)
N2—H1*N*2···O2	0.86 (2)	2.05 (2)	2.9065 (18)	173.1 (17)
N2—H2*N*2···O1	0.94 (2)	1.90 (2)	2.8432 (19)	176.2 (18)
N3—H1*N*3···O2	0.89 (2)	2.04 (2)	2.930 (2)	174 (2)
N3—H2*N*3···O1^{i}	0.91 (2)	2.11 (2)	2.913 (2)	146.9 (16)
C10—H10···O1^{ii}	0.983 (19)	2.531 (18)	3.330 (2)	138.2 (14)

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5118).

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2,3-Diaminopyridinium (2*E*,4*E*)-hexa-2,4-dienoate

Madhukar Hemamalini and Hoong-Kun Fun

S1. Comment

Non-covalent interactions, such as hydrogen bonds, $\pi\cdots\pi$ staking and the C—H$\cdots\pi$ interactions, play important roles in determining the conformation of molecules, crystal packing and molecular assembly in an organized supramolecular structure (Desiraju, 1995; Moulton & Zaworotko, 2001; Biradha & Fujita, 2002). Sorbic acid (2,4-hexadienoic acid) exhibits antibacterial and antifungal properties (Martindale, 1996) and has been used to prevent spoilage of syrup by moulds (Richards, 1972). The crystal structure of sorbic acid (Cox, 1994), 2,4-diamino-6-phenyl-1,3,5-triazine-sorbic acid (Thanigaimani *et al.*, 2007) and trimethoprim sorbate (Raj *et al.*, 2003) have been reported in the literature. Since our aim is to study some interesting hydrogen-bonding interactions, the crystal structure of the title compound is presented herein.

The asymmetric unit of the title compound, (Fig 1), contains one 2,3-diaminopyridinium cation and one sorbate anion. The bond lengths (Allen *et al.*, 1987) and angles are normal. The 2,3-diaminopyridinium cation is planar with a maximum deviation of 0.068 (2) Å for atom N3. Protonation of atom N1 has resulted in a slight increase in the magnitude of angle C1—N1—C5 [122.86 (16)°]. The sorbic acid moiety is in the *EE* configuration. The extended conformation of the sorbic acid can be described by the torsion angles C6-C7-C8-C9 = -173.77 (16)°, C7-C8-C9-C10 = 176.15 (18)°, C8-C9-C10-C11 = -176.92 (18)° and O2-C6-C7-C8 = 171.14 (16)°. This conformation is similar to that found in the trimethoprim sorbate dihydrate (Raj *et al.*, 2003).

In the crystal structure, (Fig. 2), the protonated N1 atom and the 2-amino group N atom (N2) is hydrogen-bonded to the carboxylate oxygen atoms (O1 and O2) via a pair of N1—H1N1$\cdots$O2 and N2—H2N2$\cdots$O1 hydrogen bonds forming a ring motif $R_2^2(8)$ (Bernstein *et al.*, 1995). The ion pairs are further connected via N2—H1N2$\cdots$O2^{i}; N3—H1N3$\cdots$O2^{i}; N3—H2N3$\cdots$O1^{ii} and C10—H10$\cdots$O1^{iii} hydrogen bonds (see Table 1 for symmetry codes) forming two-dimensional networks parallel to (100).

S2. Experimental

A hot methanol solution (20 ml) of 2,3-diaminopyridine (59 mg, Aldrich) and sorbic acid (56 mg, Merck) were mixed and warmed over a heating magnetic stirrer hotplate for a few minutes. The resulting solution was allowed to cool slowly at room temperature and crystals of the title compound appeared after a few days.

S3. Refinement

All H atoms were located in a difference Fourier map and refined freely [C–H = 0.94 (2)–1.04 (2) Å and N–H = 0.86 (2)–1.00 (2) Å].

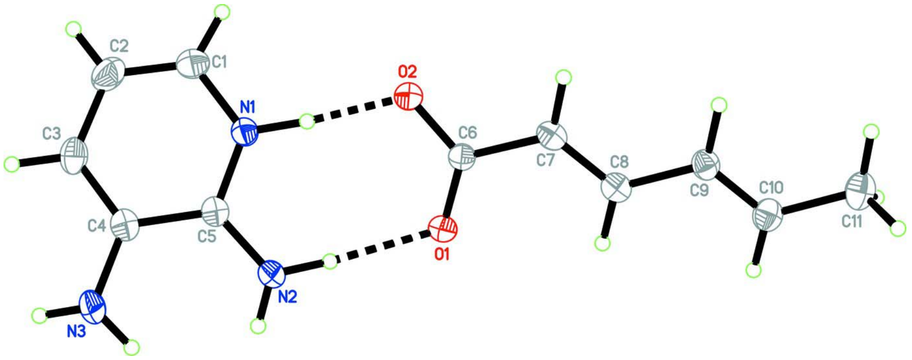

Figure 1

The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

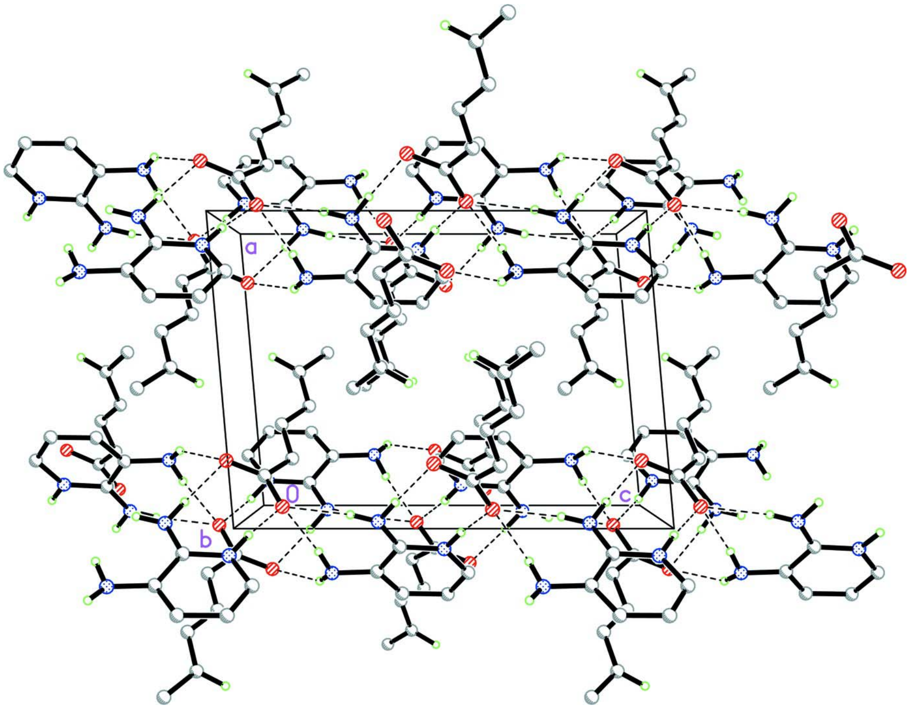

Figure 2

The crystal packing of (I) showing hydrogen bonds as dashed lines. H atoms not involved in the intermolecular interactions have been omitted for clarity.

2,3-Diaminopyridinium (2*E*,4*E*)-hexa-2,4-dienoate

Crystal data

$C_5H_8N_3^+ \cdot C_6H_7O_2^-$
$M_r = 221.26$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 9.0440$ (3) Å
$b = 10.6964$ (3) Å
$c = 12.4632$ (4) Å
$\beta = 94.947$ (2)°
$V = 1201.18$ (6) Å^3
$Z = 4$
$F(000) = 472$
$D_x = 1.224$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1444 reflections
$\theta = 3.3$–28.9°
$\mu = 0.09$ mm^{-1}

T = 296 K	0.15 × 0.15 × 0.09 mm
Block, red	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	8260 measured reflections
Radiation source: fine-focus sealed tube	2736 independent reflections
Graphite monochromator	1794 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.053
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	θ_{max} = 27.5°, θ_{min} = 2.5°
T_{min} = 0.987, T_{max} = 0.993	$h = -11 \rightarrow 8$
	$k = -13 \rightarrow 11$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.049$	All H-atom parameters refined
$wR(F^2) = 0.111$	$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 0.1735P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.02	$(\Delta/\sigma)_{\text{max}} < 0.001$
2736 reflections	$\Delta\rho_{\text{max}}$ = 0.22 e Å^{-3}
205 parameters	$\Delta\rho_{\text{min}}$ = −0.22 e Å^{-3}
0 restraints	
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
O1	−0.19667 (13)	0.14636 (12)	0.53361 (8)	0.0233 (3)
O2	−0.04642 (13)	0.18916 (12)	0.40526 (8)	0.0241 (3)
C6	−0.14500 (18)	0.12200 (17)	0.44625 (11)	0.0180 (4)
H7	−0.148 (2)	−0.0069 (18)	0.3182 (13)	0.026 (5)*
H8	−0.364 (2)	−0.0391 (18)	0.4703 (14)	0.030 (5)*
H9	−0.317 (2)	−0.1811 (18)	0.2736 (14)	0.028 (5)*
H10	−0.545 (2)	−0.2085 (19)	0.4233 (15)	0.037 (6)*
H11A	−0.672 (3)	−0.307 (2)	0.2669 (16)	0.050 (6)*
H11B	−0.556 (2)	−0.407 (2)	0.3260 (14)	0.031 (5)*
H11C	−0.507 (2)	−0.3389 (19)	0.2230 (15)	0.034 (5)*
C7	−0.1975 (2)	0.01064 (18)	0.38280 (12)	0.0224 (4)
C8	−0.3120 (2)	−0.06038 (18)	0.40571 (12)	0.0209 (4)
C9	−0.3730 (2)	−0.16160 (17)	0.33880 (13)	0.0219 (4)
C10	−0.4924 (2)	−0.22749 (18)	0.35940 (14)	0.0252 (4)

C11	−0.5606 (2)	−0.3280 (2)	0.28818 (17)	0.0309 (5)
H2N3	0.224 (2)	0.516 (2)	0.8425 (15)	0.035 (6)*
N1	0.09874 (16)	0.36086 (15)	0.52745 (10)	0.0212 (4)
N2	0.00087 (17)	0.28443 (16)	0.67865 (12)	0.0236 (4)
N3	0.1886 (2)	0.44680 (19)	0.80698 (11)	0.0286 (4)
C1	0.1867 (2)	0.43933 (19)	0.47441 (14)	0.0278 (5)
C2	0.2698 (2)	0.5265 (2)	0.52935 (15)	0.0324 (5)
C3	0.2682 (2)	0.53273 (19)	0.64186 (14)	0.0276 (5)
C4	0.18421 (19)	0.45140 (18)	0.69625 (12)	0.0222 (4)
C5	0.09207 (18)	0.36429 (17)	0.63493 (12)	0.0193 (4)
H1	0.178 (2)	0.4288 (18)	0.3983 (14)	0.027 (5)*
H2	0.324 (2)	0.586 (2)	0.4933 (15)	0.038 (6)*
H3	0.326 (2)	0.599 (2)	0.6825 (14)	0.032 (5)*
H1N1	0.039 (2)	0.297 (2)	0.4839 (15)	0.037 (6)*
H1N2	−0.021 (2)	0.291 (2)	0.7442 (17)	0.038 (6)*
H2N2	−0.065 (2)	0.236 (2)	0.6330 (16)	0.036 (6)*
H1N3	0.113 (3)	0.407 (2)	0.8330 (16)	0.049 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0270 (7)	0.0241 (8)	0.0191 (5)	−0.0026 (6)	0.0040 (5)	−0.0010 (5)
O2	0.0274 (7)	0.0258 (8)	0.0193 (5)	−0.0058 (6)	0.0023 (5)	0.0002 (5)
C6	0.0193 (9)	0.0172 (11)	0.0170 (7)	0.0011 (8)	−0.0020 (6)	0.0033 (7)
C7	0.0238 (10)	0.0241 (12)	0.0190 (7)	0.0022 (9)	0.0005 (7)	−0.0010 (7)
C8	0.0206 (9)	0.0205 (12)	0.0211 (7)	0.0050 (8)	−0.0006 (7)	0.0010 (7)
C9	0.0237 (10)	0.0191 (12)	0.0225 (8)	0.0016 (8)	0.0002 (7)	−0.0009 (7)
C10	0.0243 (10)	0.0218 (12)	0.0295 (9)	0.0013 (9)	0.0023 (7)	0.0001 (8)
C11	0.0272 (11)	0.0276 (14)	0.0373 (10)	−0.0041 (10)	−0.0007 (9)	−0.0009 (10)
N1	0.0237 (8)	0.0201 (9)	0.0197 (6)	−0.0022 (7)	0.0010 (6)	−0.0009 (6)
N2	0.0252 (9)	0.0272 (11)	0.0187 (7)	−0.0052 (8)	0.0034 (6)	−0.0046 (7)
N3	0.0309 (10)	0.0300 (11)	0.0246 (7)	−0.0088 (8)	0.0012 (7)	−0.0094 (7)
C1	0.0320 (11)	0.0280 (13)	0.0235 (8)	−0.0025 (9)	0.0033 (8)	0.0042 (8)
C2	0.0346 (12)	0.0280 (14)	0.0351 (9)	−0.0075 (10)	0.0053 (9)	0.0068 (9)
C3	0.0293 (11)	0.0183 (12)	0.0346 (9)	−0.0039 (9)	−0.0001 (8)	−0.0032 (8)
C4	0.0207 (9)	0.0206 (11)	0.0249 (8)	0.0029 (8)	0.0003 (7)	−0.0029 (8)
C5	0.0185 (9)	0.0167 (11)	0.0223 (7)	0.0030 (8)	0.0006 (6)	−0.0012 (7)

Geometric parameters (Å, º)

O1—C6	1.2488 (18)	N1—C1	1.366 (2)
O2—C6	1.285 (2)	N1—H1N1	1.00 (2)
C6—C7	1.485 (2)	N2—C5	1.336 (2)
C7—C8	1.335 (2)	N2—H1N2	0.86 (2)
C7—H7	0.974 (17)	N2—H2N2	0.95 (2)
C8—C9	1.446 (2)	N3—C4	1.378 (2)
C8—H8	0.993 (18)	N3—H2N3	0.91 (2)
C9—C10	1.333 (3)	N3—H1N3	0.89 (3)

C9—H9	1.017 (18)	C1—C2	1.347 (3)
C10—C11	1.493 (3)	C1—H1	0.952 (16)
C10—H10	0.982 (19)	C2—C3	1.405 (2)
C11—H11A	1.04 (2)	C2—H2	0.94 (2)
C11—H11B	0.97 (2)	C3—C4	1.372 (3)
C11—H11C	0.99 (2)	C3—H3	0.99 (2)
N1—C5	1.3466 (19)	C4—C5	1.427 (2)

O1—C6—O2	123.69 (16)	C1—N1—H1N1	117.8 (11)
O1—C6—C7	120.34 (15)	C5—N2—H1N2	122.4 (14)
O2—C6—C7	115.97 (14)	C5—N2—H2N2	119.2 (12)
C8—C7—C6	124.12 (15)	H1N2—N2—H2N2	115.5 (18)
C8—C7—H7	119.4 (11)	C4—N3—H2N3	116.1 (12)
C6—C7—H7	116.4 (11)	C4—N3—H1N3	115.1 (14)
C7—C8—C9	124.52 (16)	H2N3—N3—H1N3	117.3 (19)
C7—C8—H8	118.2 (11)	C2—C1—N1	120.15 (16)
C9—C8—H8	117.1 (11)	C2—C1—H1	125.5 (12)
C10—C9—C8	124.02 (16)	N1—C1—H1	114.3 (12)
C10—C9—H9	121.0 (11)	C1—C2—C3	119.12 (19)
C8—C9—H9	114.9 (11)	C1—C2—H2	121.0 (12)
C9—C10—C11	124.47 (17)	C3—C2—H2	119.8 (12)
C9—C10—H10	120.1 (12)	C4—C3—C2	121.12 (19)
C11—C10—H10	115.3 (12)	C4—C3—H3	119.4 (11)
C10—C11—H11A	109.4 (13)	C2—C3—H3	119.5 (11)
C10—C11—H11B	110.0 (11)	C3—C4—N3	123.23 (17)
H11A—C11—H11B	108.2 (17)	C3—C4—C5	118.16 (15)
C10—C11—H11C	111.7 (11)	N3—C4—C5	118.57 (17)
H11A—C11—H11C	110.2 (16)	N2—C5—N1	118.07 (16)
H11B—C11—H11C	107.3 (16)	N2—C5—C4	123.47 (15)
C5—N1—C1	122.86 (16)	N1—C5—C4	118.45 (16)
C5—N1—H1N1	119.3 (11)		

O1—C6—C7—C8	8.5 (3)	C2—C3—C4—N3	174.29 (19)
O2—C6—C7—C8	−171.14 (16)	C2—C3—C4—C5	−3.3 (3)
C6—C7—C8—C9	173.77 (16)	C1—N1—C5—N2	179.13 (17)
C7—C8—C9—C10	−176.15 (18)	C1—N1—C5—C4	−1.8 (3)
C8—C9—C10—C11	176.92 (18)	C3—C4—C5—N2	−177.03 (18)
C5—N1—C1—C2	−1.2 (3)	N3—C4—C5—N2	5.3 (3)
N1—C1—C2—C3	2.0 (3)	C3—C4—C5—N1	4.0 (3)
C1—C2—C3—C4	0.3 (3)	N3—C4—C5—N1	−173.69 (16)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*1···O2	1.00 (2)	1.66 (2)	2.6591 (19)	174.7 (18)
N2—H1*N*2···O2	0.86 (2)	2.05 (2)	2.9065 (18)	173.1 (17)
N2—H2*N*2···O1	0.94 (2)	1.90 (2)	2.8432 (19)	176.2 (18)
N3—H1*N*3···O2	0.89 (2)	2.04 (2)	2.930 (2)	174 (2)

N3—H2*N*3···O1^{i}	0.91 (2)	2.11 (2)	2.913 (2)	146.9 (16)
C10—H10···O1^{ii}	0.983 (19)	2.531 (18)	3.330 (2)	138.2 (14)

Symmetry codes: (i) $-x$, $y+1/2$, $-z+3/2$; (ii) $-x-1$, $-y$, $-z+1$.