

2,3-Diaminopyridinium sorbate–sorbic acid (1/1)

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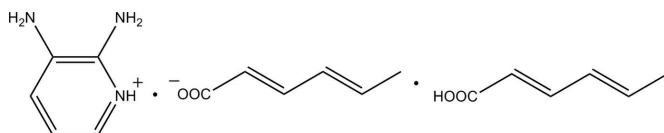
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.047; wR factor = 0.152; data-to-parameter ratio = 22.4.

In the title molecular salt–adduct, $\text{C}_5\text{H}_8\text{N}_3^+ \cdot \text{C}_6\text{H}_7\text{O}_2^- \cdot \text{C}_6\text{H}_8\text{O}_2$, the 2,3-diaminopyridinium cation is essentially planar, with a maximum deviation of 0.013 (2) Å, and is protonated at its pyridine N atom. The sorbate anion and sorbic acid molecules exist in extended conformations. In the crystal, the protonated N atom and one of the two amino-group H atoms are hydrogen bonded to the sorbate anion through a pair of $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds, forming an $R_2^2(6)$ ring motif. The carboxyl groups of the sorbic acid molecules and the carboxylate groups of the sorbate anions are connected *via* $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds. Furthermore, the ion pairs and neutral molecules are connected *via* intermolecular $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds, forming sheets lying parallel to (100).

Related literature

For a different crystal structure arising from the same synthesis conditions, see: Hemamalini & Fun (2010). For background to aminopyridines, see: Peng *et al.* (2001); Leung *et al.* (2002); Banerjee & Murugavel (2004); Lautie & Belabbes (1996). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$\text{C}_5\text{H}_8\text{N}_3^+ \cdot \text{C}_6\text{H}_7\text{O}_2^- \cdot \text{C}_6\text{H}_8\text{O}_2$
 $M_r = 333.38$

Monoclinic, $P2_1/c$
 $a = 16.1636$ (17) Å

[‡] Thomson Reuters ResearcherID: C-7576-2009.

[§] Thomson Reuters ResearcherID: A-3561-2009.

$b = 9.6538$ (10) Å
 $c = 12.6887$ (13) Å
 $\beta = 112.844$ (2)°
 $V = 1824.6$ (3) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 100$ K
 $0.47 \times 0.25 \times 0.06$ mm

Data collection

Bruker APEXII DUO CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2009)
 $T_{\min} = 0.960$, $T_{\max} = 0.994$

27805 measured reflections
5345 independent reflections
2898 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.152$
 $S = 1.02$
5345 reflections
239 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.30$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|------------------------------------------------|----------|--------------|--------------|----------------|
| $\text{O1A}-\text{H1A} \cdots \text{O1B}$ | 0.82 | 1.79 | 2.5252 (19) | 148 |
| $\text{N1}-\text{H1N1} \cdots \text{O1A}^i$ | 0.89 (3) | 2.06 (3) | 2.887 (2) | 153 (3) |
| $\text{N1}-\text{H1N1} \cdots \text{O2A}^i$ | 0.89 (3) | 2.31 (3) | 3.094 (2) | 147 (2) |
| $\text{N2}-\text{H1N2} \cdots \text{O1A}^i$ | 0.83 (2) | 2.30 (2) | 3.054 (2) | 152 (2) |
| $\text{N2}-\text{H1N2} \cdots \text{O2B}^i$ | 0.83 (2) | 2.59 (3) | 3.136 (2) | 125 (2) |
| $\text{N2}-\text{H2N2} \cdots \text{O2A}$ | 0.86 (2) | 2.00 (3) | 2.863 (2) | 177 (2) |
| $\text{N3}-\text{H1N3} \cdots \text{O2A}$ | 0.84 (2) | 2.19 (2) | 3.010 (2) | 166.1 (16) |
| $\text{N3}-\text{H2N3} \cdots \text{O2B}^{ii}$ | 0.92 (3) | 2.09 (3) | 3.002 (2) | 170 (2) |

Symmetry codes: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (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: HB6558).

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supplementary materials

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2,3-Diaminopyridinium sorbate-sorbic acid (1/1)

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Comment

Aminopyridines have recently become the focus of extensive studies, mainly because of their wide use as building blocks for synthetic transformations (Peng *et al.*, 2001; Leung *et al.*, 2002). Carboxylic acids are important in crystal engineering due to their strong and directional O—H \cdots O and N—H \cdots O hydrogen bonds; this is the main hydrogen-bonding motif often encountered in carboxylic acid–amine complexes (Banerjee & Murugavel, 2004; Lautie & Belabbes, 1996). Here, we report the synthesis and crystal structure of the title compound, (I).

The asymmetric unit of the title compound, (Fig 1), contains one 2,3-diaminopyridinium cation, one sorbate anion and one neutral sorbic acid molecule. The 2,3-diaminopyridinium cation is planar with a maximum deviation of 0.013 (2) Å for atom C2. Protonation of atom N1 has resulted in a slight increase in the angle C1—N1—C5 [123.71 (17)°]. The sorbate anion and sorbic acid moiety is in the *EE* configuration. The structure is significantly different chemically and structurally from that of the previously reported 2,3-diaminopyridinium (*2E,4E*)-hexa-2,4- dienoate compound C₅H₈N₃⁺, C₆H₇O₂⁻ (Hemamalini & Fun, 2010), even though the same synthesis was used.

In the crystal, (Fig. 2), the protonated N1 atom and the 2-amino group N atom (N2) is hydrogen-bonded to the carboxylate oxygen atoms (O1A and O2A) *via* a pair of N—H \cdots O hydrogen bonds forming a ring motif $R^1_2(6)$ (Bernstein *et al.*, 1995). The carboxyl groups of the sorbic acid molecules and the carboxylate groups of the sorbate anions are connected *via* O—H \cdots O hydrogen bonds. Furthermore, the ion pairs and neutral molecules are connected *via* N—H \cdots O hydrogen bonds (see Table 1 for symmetry codes) forming two-dimensional networks parallel to (100).

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 brown plates of the title compound appeared after a few days.

Refinement

Atoms H1N1, H1N2, H2N2, H1N3 and H2N3 were located from a difference Fourier maps and refined freely [N—H = 0.83 (2)–0.92 (2) Å]. The remaining H atoms were positioned geometrically [C—H = 0.93–0.96 Å and O—H = 0.82 Å] and were refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5 U_{\text{eq}}(\text{C})$. A rotating group model was used for the methyl group.

Figures

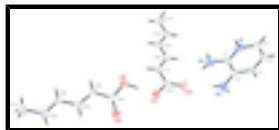


Fig. 1. The asymmetric unit of the title compound, showing 50% probability displacement ellipsoids.

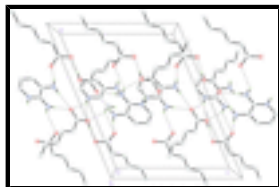


Fig. 2. The crystal packing of title compound (I).

2,3-Diaminopyridinium hexa-2,4-dienoate–hexa-2,4-dienoic acid (1/1)

Crystal data

$C_5H_8N_3^+ \cdot C_6H_7O_2^- \cdot C_6H_8O_2$

$M_r = 333.38$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 16.1636$ (17) Å

$b = 9.6538$ (10) Å

$c = 12.6887$ (13) Å

$\beta = 112.844$ (2)°

$V = 1824.6$ (3) Å³

$Z = 4$

$F(000) = 712$

$D_x = 1.214$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4699 reflections

$\theta = 2.5$ – 23.6 °

$\mu = 0.09$ mm⁻¹

$T = 100$ K

Plate, brown

$0.47 \times 0.25 \times 0.06$ mm

Data collection

Bruker APEXII DUO CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2009)

$T_{\min} = 0.960$, $T_{\max} = 0.994$

27805 measured reflections

5345 independent reflections

2898 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$

$\theta_{\max} = 30.1$ °, $\theta_{\min} = 2.5$ °

$h = -22 \rightarrow 22$

$k = -13 \rightarrow 13$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.047$

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

$wR(F^2) = 0.152$

$S = 1.02$

5345 reflections

239 parameters

0 restraints

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 0.2243P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$$

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|---------------|--------------|---------------|----------------------------------|
| N1 | 0.52439 (11) | 0.20084 (17) | 0.03419 (12) | 0.0703 (4) |
| N2 | 0.45891 (11) | 0.1854 (2) | 0.16546 (18) | 0.0778 (5) |
| N3 | 0.59685 (10) | 0.00896 (17) | 0.29774 (14) | 0.0713 (4) |
| C1 | 0.52362 (10) | 0.14816 (17) | 0.13081 (13) | 0.0563 (4) |
| C2 | 0.59314 (9) | 0.05457 (16) | 0.19419 (13) | 0.0522 (4) |
| C3 | 0.65504 (10) | 0.02052 (18) | 0.14930 (15) | 0.0642 (4) |
| H3A | 0.7001 | -0.0427 | 0.1878 | 0.077* |
| C4 | 0.65219 (12) | 0.0785 (2) | 0.04688 (16) | 0.0771 (5) |
| H4A | 0.6950 | 0.0548 | 0.0179 | 0.093* |
| C5 | 0.58688 (14) | 0.1688 (2) | -0.00887 (16) | 0.0808 (5) |
| H5A | 0.5844 | 0.2092 | -0.0766 | 0.097* |
| O1B | 0.20615 (8) | 0.22997 (14) | 0.43760 (10) | 0.0701 (3) |
| O2B | 0.26440 (7) | 0.21636 (13) | 0.62722 (10) | 0.0698 (3) |
| C6B | 0.20207 (10) | 0.24501 (15) | 0.53806 (14) | 0.0541 (4) |
| C7B | 0.11588 (10) | 0.29993 (16) | 0.53419 (14) | 0.0560 (4) |
| H7BA | 0.0703 | 0.3165 | 0.4631 | 0.067* |
| C8B | 0.10027 (10) | 0.32670 (15) | 0.62678 (13) | 0.0536 (4) |
| H8BA | 0.1460 | 0.3066 | 0.6969 | 0.064* |
| C9B | 0.01845 (10) | 0.38450 (16) | 0.62879 (14) | 0.0569 (4) |
| H9BA | -0.0277 | 0.4038 | 0.5588 | 0.068* |
| C10B | 0.00417 (13) | 0.41200 (19) | 0.72185 (16) | 0.0688 (5) |
| H10A | 0.0505 | 0.3925 | 0.7916 | 0.083* |
| C11B | -0.07969 (15) | 0.4715 (3) | 0.7250 (2) | 0.0929 (7) |

supplementary materials

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|------|--------------|---------------|--------------|------------|
| H11A | -0.1059 | 0.4066 | 0.7604 | 0.139* |
| H11B | -0.1213 | 0.4904 | 0.6485 | 0.139* |
| H11C | -0.0660 | 0.5560 | 0.7683 | 0.139* |
| O1A | 0.35766 (7) | 0.14675 (14) | 0.44960 (11) | 0.0747 (4) |
| H1A | 0.3058 | 0.1418 | 0.4452 | 0.112* |
| O2A | 0.43810 (7) | 0.06465 (17) | 0.35977 (11) | 0.0830 (4) |
| C6A | 0.36773 (10) | 0.06657 (18) | 0.37630 (13) | 0.0588 (4) |
| C7A | 0.29051 (10) | -0.02288 (17) | 0.31033 (13) | 0.0571 (4) |
| H7AA | 0.2396 | -0.0174 | 0.3273 | 0.068* |
| C8A | 0.28871 (10) | -0.10933 (17) | 0.22971 (13) | 0.0571 (4) |
| H8AA | 0.3407 | -0.1171 | 0.2153 | 0.069* |
| C9A | 0.21322 (11) | -0.19332 (17) | 0.16161 (14) | 0.0592 (4) |
| H9AA | 0.1603 | -0.1820 | 0.1733 | 0.071* |
| C10A | 0.21248 (13) | -0.28488 (19) | 0.08416 (16) | 0.0716 (5) |
| H10B | 0.2656 | -0.2947 | 0.0726 | 0.086* |
| C11A | 0.13681 (15) | -0.3735 (2) | 0.01381 (18) | 0.0891 (6) |
| H11G | 0.1245 | -0.3584 | -0.0657 | 0.134* |
| H11D | 0.0846 | -0.3507 | 0.0288 | 0.134* |
| H11E | 0.1521 | -0.4690 | 0.0325 | 0.134* |
| H1N1 | 0.4814 (17) | 0.260 (3) | -0.006 (2) | 0.112 (8)* |
| H1N2 | 0.4194 (16) | 0.234 (2) | 0.1193 (19) | 0.093 (7)* |
| H2N2 | 0.4547 (15) | 0.148 (3) | 0.225 (2) | 0.098 (9)* |
| H1N3 | 0.5524 (13) | 0.0094 (18) | 0.3168 (15) | 0.066 (5)* |
| H2N3 | 0.6417 (15) | -0.055 (3) | 0.3295 (19) | 0.104 (7)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|------|-------------|-------------|-------------|-------------|-------------|--------------|
| N1 | 0.0674 (9) | 0.0770 (10) | 0.0511 (8) | 0.0190 (8) | 0.0062 (7) | 0.0022 (7) |
| N2 | 0.0622 (9) | 0.0905 (12) | 0.0739 (11) | 0.0316 (9) | 0.0190 (8) | -0.0020 (10) |
| N3 | 0.0521 (8) | 0.0816 (11) | 0.0848 (11) | 0.0154 (8) | 0.0314 (8) | 0.0260 (9) |
| C1 | 0.0475 (8) | 0.0591 (9) | 0.0528 (9) | 0.0076 (7) | 0.0093 (6) | -0.0078 (7) |
| C2 | 0.0435 (7) | 0.0516 (8) | 0.0558 (9) | 0.0029 (6) | 0.0132 (6) | 0.0003 (7) |
| C3 | 0.0476 (8) | 0.0699 (10) | 0.0708 (11) | 0.0105 (7) | 0.0181 (7) | -0.0003 (9) |
| C4 | 0.0663 (11) | 0.1024 (15) | 0.0656 (11) | 0.0092 (10) | 0.0288 (9) | -0.0031 (11) |
| C5 | 0.0818 (13) | 0.1025 (15) | 0.0527 (10) | 0.0082 (11) | 0.0203 (9) | 0.0028 (10) |
| O1B | 0.0584 (7) | 0.0927 (9) | 0.0518 (6) | 0.0105 (6) | 0.0133 (5) | -0.0043 (6) |
| O2B | 0.0546 (6) | 0.0833 (8) | 0.0586 (7) | 0.0206 (6) | 0.0077 (5) | 0.0004 (6) |
| C6B | 0.0472 (8) | 0.0474 (8) | 0.0572 (9) | 0.0013 (6) | 0.0087 (7) | -0.0020 (7) |
| C7B | 0.0465 (8) | 0.0593 (9) | 0.0530 (9) | 0.0042 (7) | 0.0091 (6) | 0.0043 (7) |
| C8B | 0.0484 (8) | 0.0488 (8) | 0.0542 (9) | 0.0001 (6) | 0.0097 (6) | 0.0031 (7) |
| C9B | 0.0530 (8) | 0.0559 (9) | 0.0571 (9) | 0.0014 (7) | 0.0163 (7) | 0.0059 (7) |
| C10B | 0.0731 (11) | 0.0684 (11) | 0.0661 (11) | 0.0056 (9) | 0.0283 (9) | 0.0067 (9) |
| C11B | 0.0984 (15) | 0.0950 (15) | 0.1081 (17) | 0.0154 (12) | 0.0648 (13) | 0.0127 (13) |
| O1A | 0.0507 (6) | 0.0923 (9) | 0.0765 (8) | -0.0053 (6) | 0.0195 (6) | -0.0293 (7) |
| O2A | 0.0473 (6) | 0.1230 (11) | 0.0829 (9) | -0.0019 (7) | 0.0299 (6) | -0.0065 (8) |
| C6A | 0.0473 (8) | 0.0721 (10) | 0.0563 (9) | 0.0017 (7) | 0.0194 (7) | -0.0026 (8) |
| C7A | 0.0488 (8) | 0.0681 (10) | 0.0578 (9) | 0.0007 (7) | 0.0245 (7) | -0.0049 (8) |

| | | | | | | |
|------|-------------|-------------|-------------|-------------|-------------|--------------|
| C8A | 0.0536 (8) | 0.0649 (9) | 0.0525 (8) | 0.0105 (7) | 0.0201 (7) | 0.0031 (7) |
| C9A | 0.0641 (10) | 0.0571 (9) | 0.0553 (9) | 0.0064 (7) | 0.0218 (7) | -0.0006 (7) |
| C10A | 0.0771 (12) | 0.0684 (11) | 0.0646 (10) | 0.0135 (9) | 0.0222 (9) | -0.0041 (9) |
| C11A | 0.1050 (16) | 0.0634 (11) | 0.0814 (14) | 0.0037 (11) | 0.0172 (12) | -0.0159 (10) |

Geometric parameters (Å, °)

| | | | |
|--------------|-------------|----------------|-------------|
| N1—C1 | 1.332 (2) | C9B—C10B | 1.315 (2) |
| N1—C5 | 1.358 (2) | C9B—H9BA | 0.9300 |
| N1—H1N1 | 0.89 (3) | C10B—C11B | 1.487 (3) |
| N2—C1 | 1.332 (2) | C10B—H10A | 0.9300 |
| N2—H1N2 | 0.83 (2) | C11B—H11A | 0.9600 |
| N2—H2N2 | 0.86 (2) | C11B—H11B | 0.9600 |
| N3—C2 | 1.365 (2) | C11B—H11C | 0.9600 |
| N3—H1N3 | 0.843 (18) | O1A—C6A | 1.2682 (19) |
| N3—H2N3 | 0.92 (2) | O1A—H1A | 0.8200 |
| C1—C2 | 1.423 (2) | O2A—C6A | 1.2341 (18) |
| C2—C3 | 1.370 (2) | C6A—C7A | 1.481 (2) |
| C3—C4 | 1.399 (3) | C7A—C8A | 1.312 (2) |
| C3—H3A | 0.9300 | C7A—H7AA | 0.9300 |
| C4—C5 | 1.339 (3) | C8A—C9A | 1.440 (2) |
| C4—H4A | 0.9300 | C8A—H8AA | 0.9300 |
| C5—H5A | 0.9300 | C9A—C10A | 1.318 (2) |
| O1B—C6B | 1.310 (2) | C9A—H9AA | 0.9300 |
| O2B—C6B | 1.2192 (17) | C10A—C11A | 1.475 (3) |
| C6B—C7B | 1.474 (2) | C10A—H10B | 0.9300 |
| C7B—C8B | 1.319 (2) | C11A—H11G | 0.9600 |
| C7B—H7BA | 0.9300 | C11A—H11D | 0.9600 |
| C8B—C9B | 1.445 (2) | C11A—H11E | 0.9600 |
| C8B—H8BA | 0.9300 | | |
| C1—N1—C5 | 123.90 (16) | C10B—C9B—H9BA | 117.5 |
| C1—N1—H1N1 | 119.1 (16) | C8B—C9B—H9BA | 117.5 |
| C5—N1—H1N1 | 117.0 (16) | C9B—C10B—C11B | 125.59 (18) |
| C1—N2—H1N2 | 114.2 (15) | C9B—C10B—H10A | 117.2 |
| C1—N2—H2N2 | 120.9 (16) | C11B—C10B—H10A | 117.2 |
| H1N2—N2—H2N2 | 124 (2) | C10B—C11B—H11A | 109.5 |
| C2—N3—H1N3 | 123.5 (12) | C10B—C11B—H11B | 109.5 |
| C2—N3—H2N3 | 111.8 (14) | H11A—C11B—H11B | 109.5 |
| H1N3—N3—H2N3 | 119.6 (19) | C10B—C11B—H11C | 109.5 |
| N2—C1—N1 | 119.33 (16) | H11A—C11B—H11C | 109.5 |
| N2—C1—C2 | 122.29 (17) | H11B—C11B—H11C | 109.5 |
| N1—C1—C2 | 118.38 (15) | C6A—O1A—H1A | 109.5 |
| N3—C2—C3 | 123.83 (15) | O2A—C6A—O1A | 121.53 (16) |
| N3—C2—C1 | 118.61 (14) | O2A—C6A—C7A | 121.69 (15) |
| C3—C2—C1 | 117.49 (15) | O1A—C6A—C7A | 116.77 (13) |
| C2—C3—C4 | 121.61 (16) | C8A—C7A—C6A | 124.78 (14) |
| C2—C3—H3A | 119.2 | C8A—C7A—H7AA | 117.6 |
| C4—C3—H3A | 119.2 | C6A—C7A—H7AA | 117.6 |
| C5—C4—C3 | 119.07 (17) | C7A—C8A—C9A | 125.68 (15) |

supplementary materials

| | | | |
|--------------|--------------|-------------------|--------------|
| C5—C4—H4A | 120.5 | C7A—C8A—H8AA | 117.2 |
| C3—C4—H4A | 120.5 | C9A—C8A—H8AA | 117.2 |
| C4—C5—N1 | 119.52 (19) | C10A—C9A—C8A | 125.81 (17) |
| C4—C5—H5A | 120.2 | C10A—C9A—H9AA | 117.1 |
| N1—C5—H5A | 120.2 | C8A—C9A—H9AA | 117.1 |
| O2B—C6B—O1B | 122.84 (14) | C9A—C10A—C11A | 127.25 (19) |
| O2B—C6B—C7B | 122.85 (15) | C9A—C10A—H10B | 116.4 |
| O1B—C6B—C7B | 114.30 (13) | C11A—C10A—H10B | 116.4 |
| C8B—C7B—C6B | 123.09 (14) | C10A—C11A—H11G | 109.5 |
| C8B—C7B—H7BA | 118.5 | C10A—C11A—H11D | 109.5 |
| C6B—C7B—H7BA | 118.5 | H11G—C11A—H11D | 109.5 |
| C7B—C8B—C9B | 125.75 (14) | C10A—C11A—H11E | 109.5 |
| C7B—C8B—H8BA | 117.1 | H11G—C11A—H11E | 109.5 |
| C9B—C8B—H8BA | 117.1 | H11D—C11A—H11E | 109.5 |
| C10B—C9B—C8B | 125.09 (16) | | |
| C5—N1—C1—N2 | -179.49 (19) | O2B—C6B—C7B—C8B | 2.3 (2) |
| C5—N1—C1—C2 | 1.2 (3) | O1B—C6B—C7B—C8B | -177.53 (15) |
| N2—C1—C2—N3 | -4.5 (3) | C6B—C7B—C8B—C9B | 177.96 (14) |
| N1—C1—C2—N3 | 174.80 (15) | C7B—C8B—C9B—C10B | -179.26 (17) |
| N2—C1—C2—C3 | 178.37 (17) | C8B—C9B—C10B—C11B | 179.96 (18) |
| N1—C1—C2—C3 | -2.3 (2) | O2A—C6A—C7A—C8A | -0.6 (3) |
| N3—C2—C3—C4 | -174.93 (17) | O1A—C6A—C7A—C8A | 178.42 (16) |
| C1—C2—C3—C4 | 2.0 (2) | C6A—C7A—C8A—C9A | -177.50 (15) |
| C2—C3—C4—C5 | -0.5 (3) | C7A—C8A—C9A—C10A | -176.71 (18) |
| C3—C4—C5—N1 | -0.8 (3) | C8A—C9A—C10A—C11A | 179.34 (18) |
| C1—N1—C5—C4 | 0.4 (3) | | |

Hydrogen-bond geometry (\AA , $^\circ$)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O1A—H1A \cdots O1B | 0.82 | 1.79 | 2.5252 (19) | 148 |
| N1—H1N1 \cdots O1A ⁱ | 0.89 (3) | 2.06 (3) | 2.887 (2) | 153 (3) |
| N1—H1N1 \cdots O2A ⁱ | 0.89 (3) | 2.31 (3) | 3.094 (2) | 147 (2) |
| N2—H1N2 \cdots O1A ⁱ | 0.83 (2) | 2.30 (2) | 3.054 (2) | 152 (2) |
| N2—H1N2 \cdots O2B ⁱ | 0.83 (2) | 2.59 (3) | 3.136 (2) | 125 (2) |
| N2—H2N2 \cdots O2A | 0.86 (2) | 2.00 (3) | 2.863 (2) | 177 (2) |
| N3—H1N3 \cdots O2A | 0.84 (2) | 2.19 (2) | 3.010 (2) | 166.1 (16) |
| N3—H2N3 \cdots O2B ⁱⁱ | 0.92 (3) | 2.09 (3) | 3.002 (2) | 170 (2) |

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

Fig. 1

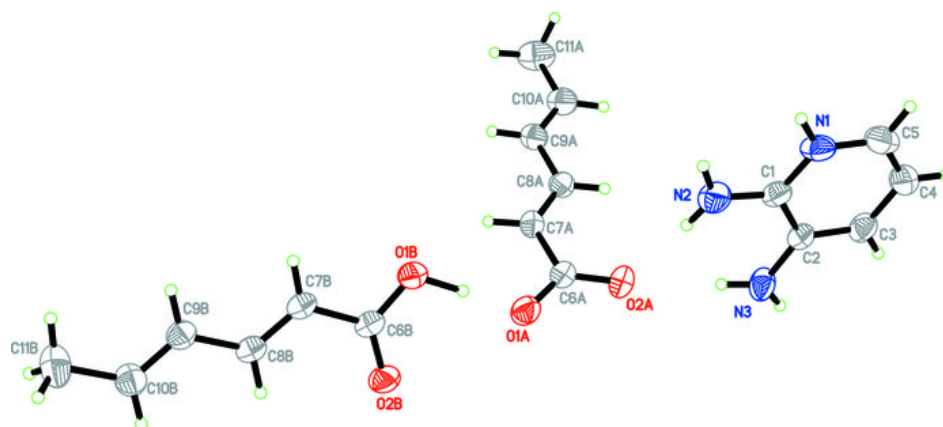


Fig. 2

