# organic compounds

# 2-Amino-4-methylpyridinium 2-hydroxy-benzoate

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The asymmetric unit of the title molecular salt, $C_6H_9N_2^+\cdot C_7H_5O_3^-$, contains two cations and two anions. Both the salicylate anions contain an intramolecular $O-H\cdots O$ hydrogen bond, which generates an $S(6)$ ring. Both the 2-amino-4-methylpyridine molecules are protonated at their pyridine N atoms. In the crystal, both cations form two $N-H\cdots O$ hydrogen bonds to their adjacent anions, forming ion pairs. Further $N-H\cdots O$ links generate sheets lying parallel to the $ab$ plane. In addition, weak $C-H\cdots O$ bonds and aromatic $\pi-\pi$ stacking interactions [centroid–centroid distances = 3.5691 (9) and 3.6215 (9) Å] are observed between the cations and anions.

## Related literature

For related structures, see: Navarro Ranninger *et al.* (1985); Luque *et al.* (1997); Qin *et al.* (1999); Jin *et al.* (2001); Albrecht *et al.* (2003); Kvick & Noordik (1977). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).
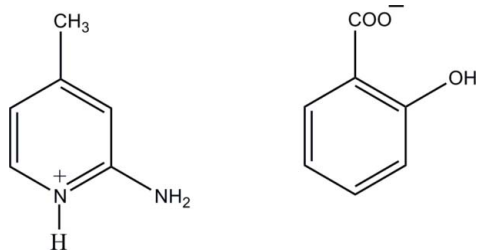
## Experimental

### Crystal data

| | |
|---|---|
| $C_6H_9N_2^+\cdot C_7H_5O_3^-$ | $\gamma$ = 88.824 (2)° |
| $M_r$ = 246.26 | $V$ = 1238.58 (5) Å³ |
| Triclinic, $P\bar{1}$ | $Z$ = 4 |
| $a$ = 7.2417 (2) Å | Mo $K\alpha$ radiation |
| $b$ = 12.5520 (3) Å | $\mu$ = 0.10 mm⁻¹ |
| $c$ = 14.7699 (3) Å | $T$ = 100 K |
| $\alpha$ = 68.752 (2)° | 0.32 × 0.10 × 0.04 mm |
| $\beta$ = 82.038 (2)° | |

### Data collection

| | |
|---|---|
| Bruker APEXII CCD diffractometer | 23090 measured reflections |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2009) | 8280 independent reflections |
| $T_{min}$ = 0.971, $T_{max}$ = 0.996 | 5112 reflections with $I > 2\sigma(I)$ |
| | $R_{int}$ = 0.047 |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.056 | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2)$ = 0.155 | |
| $S$ = 1.00 | |
| 8280 reflections | $\Delta\rho_{max}$ = 0.38 e Å⁻³ |
| 359 parameters | $\Delta\rho_{min}$ = −0.28 e Å⁻³ |

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|---|---|---|---|
| $O3A-H1A3\cdots O2A$ | 0.99 (2) | 1.61 (2) | 2.5310 (16) | 154 (2) |
| $N1A-H1NA\cdots O1B^{i}$ | 0.99 (2) | 1.71 (2) | 2.6965 (17) | 174 (2) |
| $N2A-H2NA\cdots O1A^{ii}$ | 0.90 (2) | 1.99 (2) | 2.8645 (19) | 164 (2) |
| $O3B-H1B3\cdots O2B$ | 0.94 (3) | 1.62 (3) | 2.5179 (16) | 158 (2) |
| $N2A-H3NA\cdots O2B^{i}$ | 0.94 (2) | 1.91 (2) | 2.8468 (18) | 178 (2) |
| $N1B-H1NB\cdots O2A$ | 0.96 (2) | 1.76 (2) | 2.7186 (17) | 172.7 (17) |
| $N2B-H2NB\cdots O1A$ | 0.96 (2) | 1.84 (2) | 2.7976 (18) | 177.0 (16) |
| $N2B-H3NB\cdots O1B^{iii}$ | 0.93 (2) | 1.88 (2) | 2.8097 (19) | 174.3 (13) |
| $C8B-H8BA\cdots O2B^{iv}$ | 0.93 | 2.47 | 3.357 (2) | 159 |
| $C10B-H10B\cdots O3B$ | 0.93 | 2.38 | 3.039 (2) | 128 |

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

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).

‡ Thomson Reuters ResearcherID: A-3561-2009.

# organic compounds

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# supporting information

## 2-Amino-4-methylpyridinium 2-hydroxybenzoate

### Madhukar Hemamalini and Hoong-Kun Fun

### S1. Comment

There are numerous examples of 2-amino-substituted pyridine compounds in which the 2-aminopyridines act as neutral ligands (Navarro Ranninger *et al.*, 1985; Luque *et al.*, 1997; Qin *et al.*, 1999) or as protonated cations (Luque *et al.*, 1997; Jin *et al.*, 2001; Albrecht *et al.*, 2003). In order to study some hydrogen bonding interactions, the synthesis and structure of the title salt, (I), is presented here.

The asymmetric unit of the title compound consists of two crystallographically independent 2-amino-4-methyl-pyridinium cations (A and B) and two salicylate anions (A and B) (Fig. 1). Each 2-amino-4-methylpyridinium cation is planar, with a maximum deviation of 0.004 (1) Å for atom N1A in cation A and 0.006 (2) Å for atom C11B in cation B. In the cations, protonation at atoms N1A and N1B lead to a slight increase in the C9A—N1A—C10A [122.06 (14)°] and C9B—N1B—C10B [121.76 (13)°] angles compared to those observed in an unprotonated structure (Kvick & Noordik, 1977). The bond lengths (Allen *et al.*, 1987) and angles are normal.

In the crystal structure (Fig. 2), the carboxylate groups of each salicylate anions interact with the corresponding 2-amino-4-methylpyridinium cations via a pair of N—H···O hydrogen bonds forming an $R_2^2(8)$ ring motif (Bernstein *et al.*, 1995). Furthermore, these motifs are connected via N—H···O hydrogen bonds, forming a two-dimensional network parallel to the *ab*-plane. There is an intramolecular O—H···O hydrogen bond in the salicylate anions, which generates an $S(6)$ ring motif. In addition, weak C—H···O and $\pi$–$\pi$ interactions are observed between the cation-anion pairs, [Cg1(N1A/C8A–C12A)& Cg4(C1A–C6A)] and [Cg2(N1B/C8B–C12B) & Cg3(C1B–C6B)], with centroid-centroid distances of 3.5691 (9) Å (1+x, y, z) and 3.6215 (9) Å (-1+x, y, z), respectively.

### S2. Experimental

A hot methanol solution (20 ml) of 2-amino-4-methylpyridine (54 mg, Aldrich) and salicylic acid (69 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 colourless needles of (I) appeared after a few days.

### S3. Refinement

Atoms H1A3, H1B3,H1NA, H2NA, H3NA, H1NB, H2NB, H3NB were located from a difference Fourier map and were refined freely [N–H= 0.90 (2)– 0.99(20 Å and O–H =0.94 (2)–0.99 (2) Å]. The remaining hydrogen atoms were positioned geometrically [C–H = 0.93 or 0.96 Å] and were refined using a riding model, with $U_{iso}$(H) = 1.2 or 1.5 $U_{eq}$(C). A rotating group model was used for the methyl group.
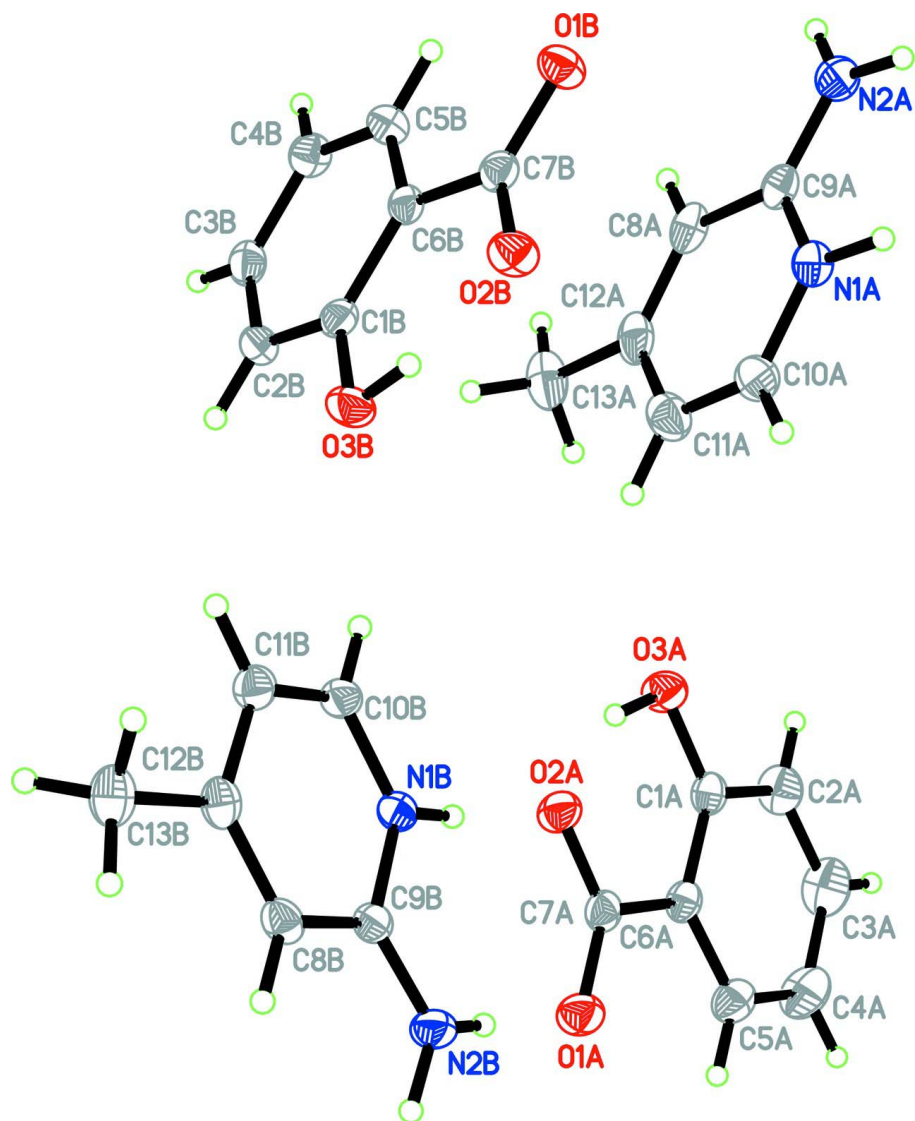
**Figure 1**
The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level.
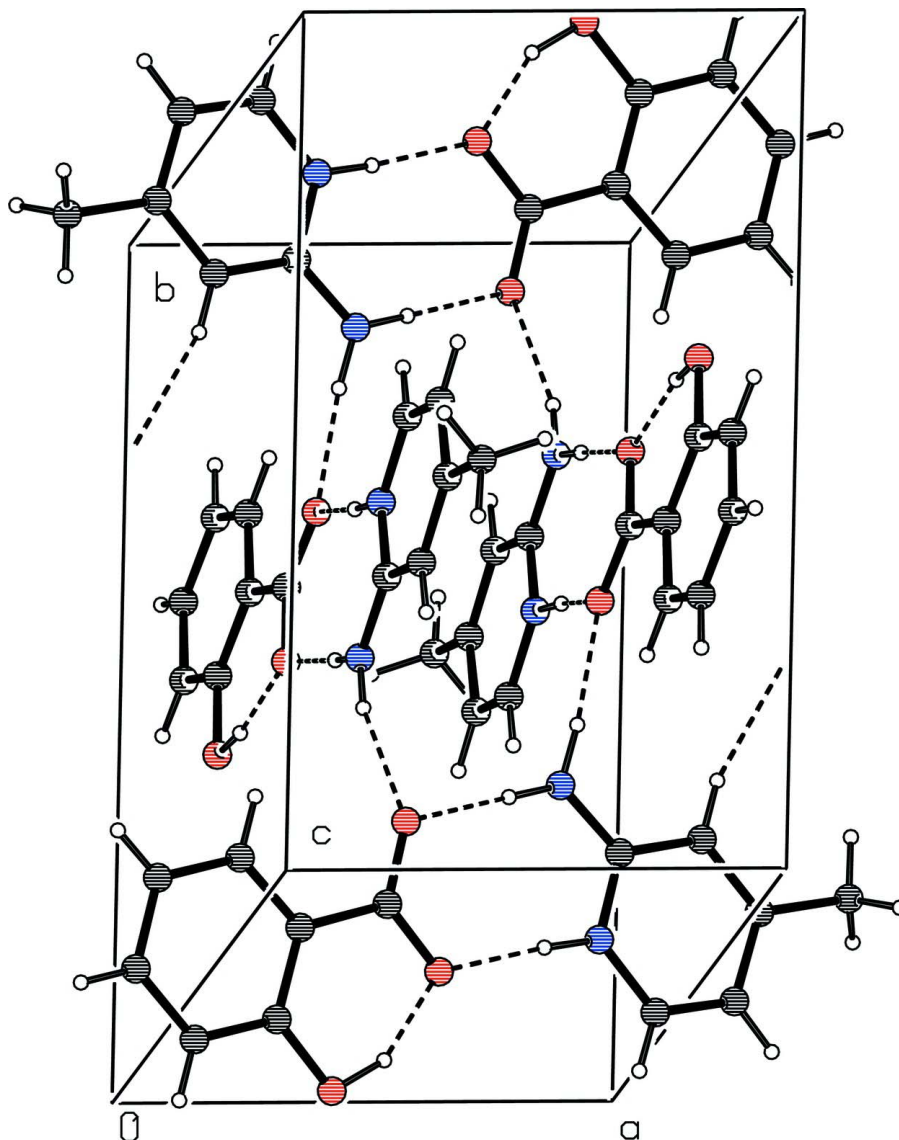
**Figure 2**

Hydrogen bonding patterns in compound (I).

**2-Amino-4-methylpyridinium 2-hydroxybenzoate**

*Crystal data*

| | |
|---|---|
| $C_6H_9N_2{}^+ \cdot C_7H_5O_3{}^-$ | $Z = 4$ |
| $M_r = 246.26$ | $F(000) = 520$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.321$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 7.2417$ (2) Å | Cell parameters from 3981 reflections |
| $b = 12.5520$ (3) Å | $\theta = 2.7–31.4°$ |
| $c = 14.7699$ (3) Å | $\mu = 0.10$ mm$^{-1}$ |
| $\alpha = 68.752$ (2)° | $T = 100$ K |
| $\beta = 82.038$ (2)° | Needle, colourless |
| $\gamma = 88.824$ (2)° | $0.32 \times 0.10 \times 0.04$ mm |
| $V = 1238.58$ (5) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker APEXII CCD diffractometer | 23090 measured reflections |
| Radiation source: fine-focus sealed tube | 8280 independent reflections |
| Graphite monochromator | 5112 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{int} = 0.047$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2009) | $\theta_{max} = 31.6°$, $\theta_{min} = 1.5°$ |
| | $h = -10 \rightarrow 10$ |
| $T_{min} = 0.971$, $T_{max} = 0.996$ | $k = -15 \rightarrow 18$ |
| | $l = -21 \rightarrow 21$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.056$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.155$ | |
| $S = 1.00$ | H atoms treated by a mixture of independent and constrained refinement |
| 8280 reflections | |
| 359 parameters | $w = 1/[\sigma^2(F_o^2) + (0.0755P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 0 restraints | |
| Primary atom site location: structure-invariant direct methods | $(\Delta/\sigma)_{max} < 0.001$ |
| | $\Delta\rho_{max} = 0.38$ e Å$^{-3}$ |
| | $\Delta\rho_{min} = -0.28$ e Å$^{-3}$ |

*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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| O1A | 0.68689 (15) | −0.11656 (9) | 0.22307 (8) | 0.0266 (3) |
| O2A | 0.61939 (14) | 0.06247 (9) | 0.20906 (8) | 0.0243 (2) |
| O3A | 0.85815 (16) | 0.22440 (9) | 0.12227 (8) | 0.0255 (2) |
| C1A | 0.9761 (2) | 0.14446 (13) | 0.10815 (11) | 0.0204 (3) |
| C2A | 1.1562 (2) | 0.18050 (15) | 0.05960 (12) | 0.0290 (4) |
| H2AA | 1.1918 | 0.2575 | 0.0369 | 0.035* |
| C3A | 1.2811 (2) | 0.10169 (17) | 0.04530 (13) | 0.0366 (4) |
| H3AA | 1.4012 | 0.1260 | 0.0133 | 0.044* |
| C4A | 1.2299 (2) | −0.01322 (16) | 0.07799 (13) | 0.0350 (4) |
| H4AA | 1.3150 | −0.0660 | 0.0684 | 0.042* |
| C5A | 1.0506 (2) | −0.04874 (14) | 0.12505 (12) | 0.0263 (3) |
| H5AA | 1.0156 | −0.1257 | 0.1462 | 0.032* |
| C6A | 0.9217 (2) | 0.02859 (13) | 0.14131 (10) | 0.0198 (3) |
| C7A | 0.7306 (2) | −0.01258 (12) | 0.19453 (11) | 0.0200 (3) |

| | | | |
|---|---|---|---|
| N1A | 0.68931 (17) | 0.46245 (11) | 0.40308 (10) | 0.0214 (3) |
| N2A | 0.74130 (19) | 0.65677 (12) | 0.35534 (11) | 0.0247 (3) |
| C8A | 0.6621 (2) | 0.57734 (14) | 0.23833 (11) | 0.0239 (3) |
| H8AA | 0.6670 | 0.6489 | 0.1885 | 0.029* |
| C9A | 0.6984 (2) | 0.56827 (13) | 0.33225 (11) | 0.0207 (3) |
| C10A | 0.6458 (2) | 0.36749 (13) | 0.38600 (12) | 0.0243 (3) |
| H10A | 0.6395 | 0.2966 | 0.4368 | 0.029* |
| C11A | 0.6114 (2) | 0.37414 (15) | 0.29629 (13) | 0.0281 (4) |
| H11A | 0.5826 | 0.3084 | 0.2852 | 0.034* |
| C12A | 0.6199 (2) | 0.48242 (15) | 0.21964 (12) | 0.0257 (3) |
| C13A | 0.5855 (2) | 0.49005 (17) | 0.11939 (13) | 0.0338 (4) |
| H13A | 0.6056 | 0.5677 | 0.0745 | 0.051* |
| H13B | 0.4593 | 0.4655 | 0.1225 | 0.051* |
| H13C | 0.6698 | 0.4417 | 0.0971 | 0.051* |
| O1B | 0.24453 (15) | 0.57634 (9) | 0.41257 (8) | 0.0228 (2) |
| O2B | 0.17672 (15) | 0.39175 (8) | 0.45092 (8) | 0.0239 (2) |
| O3B | 0.08596 (16) | 0.31742 (9) | 0.32564 (9) | 0.0257 (3) |
| C1B | 0.10480 (19) | 0.42674 (12) | 0.26094 (11) | 0.0192 (3) |
| C2B | 0.0707 (2) | 0.44786 (13) | 0.16487 (12) | 0.0223 (3) |
| H2BA | 0.0358 | 0.3880 | 0.1471 | 0.027* |
| C3B | 0.0891 (2) | 0.55775 (13) | 0.09701 (11) | 0.0229 (3) |
| H3BA | 0.0664 | 0.5716 | 0.0333 | 0.027* |
| C4B | 0.1412 (2) | 0.64860 (13) | 0.12204 (11) | 0.0234 (3) |
| H4BA | 0.1538 | 0.7225 | 0.0755 | 0.028* |
| C5B | 0.1739 (2) | 0.62728 (13) | 0.21704 (11) | 0.0212 (3) |
| H5BA | 0.2080 | 0.6878 | 0.2340 | 0.025* |
| C6B | 0.15685 (19) | 0.51694 (12) | 0.28802 (11) | 0.0174 (3) |
| C7B | 0.19489 (19) | 0.49451 (12) | 0.39042 (11) | 0.0183 (3) |
| N1B | 0.26797 (18) | −0.00016 (10) | 0.30554 (9) | 0.0190 (3) |
| N2B | 0.34027 (19) | −0.18896 (11) | 0.33877 (10) | 0.0242 (3) |
| C8B | 0.0346 (2) | −0.14199 (13) | 0.40050 (11) | 0.0202 (3) |
| H8BA | −0.0036 | −0.2186 | 0.4305 | 0.024* |
| C9B | 0.2159 (2) | −0.11240 (12) | 0.34789 (11) | 0.0188 (3) |
| C10B | 0.1505 (2) | 0.08329 (12) | 0.31225 (11) | 0.0203 (3) |
| H10B | 0.1904 | 0.1595 | 0.2817 | 0.024* |
| C11B | −0.0243 (2) | 0.05709 (13) | 0.36292 (11) | 0.0218 (3) |
| H11B | −0.1028 | 0.1148 | 0.3680 | 0.026* |
| C12B | −0.0857 (2) | −0.05856 (13) | 0.40769 (10) | 0.0207 (3) |
| C13B | −0.2817 (2) | −0.08836 (15) | 0.46052 (12) | 0.0277 (4) |
| H13D | −0.2952 | −0.1695 | 0.4954 | 0.042* |
| H13E | −0.3683 | −0.0649 | 0.4138 | 0.042* |
| H13F | −0.3067 | −0.0497 | 0.5061 | 0.042* |
| H1A3 | 0.743 (3) | 0.1794 (19) | 0.1574 (17) | 0.061 (7)* |
| H1NA | 0.719 (3) | 0.4528 (17) | 0.4688 (16) | 0.049 (6)* |
| H2NA | 0.748 (3) | 0.7276 (17) | 0.3090 (14) | 0.035 (5)* |
| H1B3 | 0.111 (3) | 0.327 (2) | 0.3833 (18) | 0.063 (7)* |
| H3NA | 0.769 (3) | 0.6423 (17) | 0.4187 (16) | 0.044 (6)* |
| H1NB | 0.390 (3) | 0.0191 (17) | 0.2677 (14) | 0.046 (6)* |

| | | | |
|---|---|---|---|
| H2NB | 0.457 (3) | −0.1645 (16) | 0.2974 (14) | 0.039 (5)* |
| H3NB | 0.302 (2) | −0.2656 (16) | 0.3608 (13) | 0.029 (5)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1A | 0.0262 (6) | 0.0192 (5) | 0.0306 (6) | −0.0005 (4) | −0.0029 (5) | −0.0047 (5) |
| O2A | 0.0183 (5) | 0.0199 (5) | 0.0321 (6) | 0.0006 (4) | −0.0010 (4) | −0.0071 (5) |
| O3A | 0.0233 (6) | 0.0201 (5) | 0.0297 (6) | −0.0014 (4) | 0.0001 (5) | −0.0061 (5) |
| C1A | 0.0193 (7) | 0.0240 (7) | 0.0168 (7) | 0.0010 (6) | −0.0036 (6) | −0.0057 (6) |
| C2A | 0.0231 (8) | 0.0311 (9) | 0.0268 (9) | −0.0053 (7) | 0.0022 (6) | −0.0052 (7) |
| C3A | 0.0234 (8) | 0.0492 (11) | 0.0310 (10) | −0.0004 (8) | 0.0051 (7) | −0.0104 (8) |
| C4A | 0.0281 (9) | 0.0431 (10) | 0.0323 (10) | 0.0099 (8) | 0.0014 (7) | −0.0145 (8) |
| C5A | 0.0272 (8) | 0.0280 (8) | 0.0239 (8) | 0.0064 (6) | −0.0042 (6) | −0.0099 (7) |
| C6A | 0.0192 (7) | 0.0234 (7) | 0.0162 (7) | 0.0026 (6) | −0.0040 (5) | −0.0062 (6) |
| C7A | 0.0208 (7) | 0.0206 (7) | 0.0176 (7) | 0.0015 (6) | −0.0063 (6) | −0.0046 (6) |
| N1A | 0.0196 (6) | 0.0233 (6) | 0.0208 (7) | 0.0000 (5) | −0.0031 (5) | −0.0073 (5) |
| N2A | 0.0277 (7) | 0.0210 (7) | 0.0242 (7) | 0.0021 (5) | −0.0069 (6) | −0.0057 (6) |
| C8A | 0.0165 (7) | 0.0309 (8) | 0.0208 (8) | 0.0033 (6) | −0.0028 (6) | −0.0052 (6) |
| C9A | 0.0137 (6) | 0.0239 (7) | 0.0227 (8) | 0.0024 (5) | −0.0021 (6) | −0.0067 (6) |
| C10A | 0.0216 (7) | 0.0223 (7) | 0.0279 (8) | −0.0023 (6) | −0.0024 (6) | −0.0079 (6) |
| C11A | 0.0218 (8) | 0.0332 (9) | 0.0330 (9) | −0.0034 (7) | −0.0017 (7) | −0.0171 (7) |
| C12A | 0.0136 (7) | 0.0395 (9) | 0.0255 (8) | 0.0008 (6) | −0.0022 (6) | −0.0138 (7) |
| C13A | 0.0239 (8) | 0.0534 (11) | 0.0275 (9) | −0.0020 (8) | −0.0040 (7) | −0.0185 (8) |
| O1B | 0.0295 (6) | 0.0175 (5) | 0.0216 (6) | −0.0026 (4) | −0.0058 (4) | −0.0065 (4) |
| O2B | 0.0298 (6) | 0.0162 (5) | 0.0225 (6) | −0.0027 (4) | −0.0036 (5) | −0.0030 (4) |
| O3B | 0.0318 (6) | 0.0153 (5) | 0.0302 (6) | −0.0019 (4) | −0.0077 (5) | −0.0070 (5) |
| C1B | 0.0150 (6) | 0.0170 (7) | 0.0252 (8) | 0.0019 (5) | −0.0024 (6) | −0.0073 (6) |
| C2B | 0.0196 (7) | 0.0245 (7) | 0.0280 (8) | 0.0012 (6) | −0.0054 (6) | −0.0149 (7) |
| C3B | 0.0193 (7) | 0.0297 (8) | 0.0222 (8) | 0.0031 (6) | −0.0055 (6) | −0.0117 (7) |
| C4B | 0.0238 (8) | 0.0223 (7) | 0.0218 (8) | 0.0008 (6) | −0.0036 (6) | −0.0053 (6) |
| C5B | 0.0226 (7) | 0.0194 (7) | 0.0225 (8) | −0.0010 (6) | −0.0032 (6) | −0.0087 (6) |
| C6B | 0.0132 (6) | 0.0180 (7) | 0.0207 (7) | 0.0000 (5) | −0.0024 (5) | −0.0067 (6) |
| C7B | 0.0152 (7) | 0.0174 (7) | 0.0209 (7) | 0.0010 (5) | −0.0016 (5) | −0.0058 (6) |
| N1B | 0.0184 (6) | 0.0159 (6) | 0.0217 (6) | −0.0014 (5) | −0.0032 (5) | −0.0053 (5) |
| N2B | 0.0221 (7) | 0.0158 (6) | 0.0330 (8) | −0.0004 (5) | −0.0030 (6) | −0.0071 (6) |
| C8B | 0.0214 (7) | 0.0181 (7) | 0.0188 (7) | −0.0048 (6) | −0.0033 (6) | −0.0034 (6) |
| C9B | 0.0216 (7) | 0.0162 (7) | 0.0185 (7) | −0.0001 (5) | −0.0066 (6) | −0.0048 (6) |
| C10B | 0.0235 (7) | 0.0160 (7) | 0.0214 (7) | 0.0010 (6) | −0.0067 (6) | −0.0056 (6) |
| C11B | 0.0229 (8) | 0.0229 (7) | 0.0216 (8) | 0.0035 (6) | −0.0066 (6) | −0.0093 (6) |
| C12B | 0.0208 (7) | 0.0264 (8) | 0.0148 (7) | −0.0008 (6) | −0.0056 (6) | −0.0061 (6) |
| C13B | 0.0202 (8) | 0.0356 (9) | 0.0251 (8) | −0.0018 (7) | −0.0020 (6) | −0.0087 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1A—C7A | 1.2500 (18) | O1B—C7B | 1.2580 (17) |
| O2A—C7A | 1.2843 (16) | O2B—C7B | 1.2722 (17) |
| O3A—C1A | 1.3591 (17) | O3B—C1B | 1.3549 (18) |

| | | | |
|---|---|---|---|
| O3A—H1A3 | 0.99 (2) | O3B—H1B3 | 0.94 (2) |
| C1A—C2A | 1.396 (2) | C1B—C2B | 1.402 (2) |
| C1A—C6A | 1.402 (2) | C1B—C6B | 1.404 (2) |
| C2A—C3A | 1.380 (2) | C2B—C3B | 1.376 (2) |
| C2A—H2AA | 0.9300 | C2B—H2BA | 0.9300 |
| C3A—C4A | 1.385 (3) | C3B—C4B | 1.393 (2) |
| C3A—H3AA | 0.9300 | C3B—H3BA | 0.9300 |
| C4A—C5A | 1.384 (2) | C4B—C5B | 1.383 (2) |
| C4A—H4AA | 0.9300 | C4B—H4BA | 0.9300 |
| C5A—C6A | 1.3933 (19) | C5B—C6B | 1.397 (2) |
| C5A—H5AA | 0.9300 | C5B—H5BA | 0.9300 |
| C6A—C7A | 1.495 (2) | C6B—C7B | 1.499 (2) |
| N1A—C10A | 1.356 (2) | N1B—C9B | 1.3550 (18) |
| N1A—C9A | 1.3566 (19) | N1B—C10B | 1.3584 (18) |
| N1A—H1NA | 0.99 (2) | N1B—H1NB | 0.96 (2) |
| N2A—C9A | 1.329 (2) | N2B—C9B | 1.3331 (18) |
| N2A—H2NA | 0.90 (2) | N2B—H2NB | 0.96 (2) |
| N2A—H3NA | 0.93 (2) | N2B—H3NB | 0.930 (19) |
| C8A—C12A | 1.366 (2) | C8B—C12B | 1.373 (2) |
| C8A—C9A | 1.411 (2) | C8B—C9B | 1.412 (2) |
| C8A—H8AA | 0.9300 | C8B—H8BA | 0.9300 |
| C10A—C11A | 1.355 (2) | C10B—C11B | 1.359 (2) |
| C10A—H10A | 0.9300 | C10B—H10B | 0.9300 |
| C11A—C12A | 1.415 (2) | C11B—C12B | 1.411 (2) |
| C11A—H11A | 0.9300 | C11B—H11B | 0.9300 |
| C12A—C13A | 1.504 (2) | C12B—C13B | 1.506 (2) |
| C13A—H13A | 0.9600 | C13B—H13D | 0.9600 |
| C13A—H13B | 0.9600 | C13B—H13E | 0.9600 |
| C13A—H13C | 0.9600 | C13B—H13F | 0.9600 |
| | | | |
| C1A—O3A—H1A3 | 103.3 (12) | C1B—O3B—H1B3 | 101.2 (14) |
| O3A—C1A—C2A | 118.13 (14) | O3B—C1B—C2B | 117.87 (13) |
| O3A—C1A—C6A | 121.82 (13) | O3B—C1B—C6B | 121.75 (13) |
| C2A—C1A—C6A | 120.05 (14) | C2B—C1B—C6B | 120.38 (13) |
| C3A—C2A—C1A | 119.90 (16) | C3B—C2B—C1B | 119.53 (13) |
| C3A—C2A—H2AA | 120.0 | C3B—C2B—H2BA | 120.2 |
| C1A—C2A—H2AA | 120.0 | C1B—C2B—H2BA | 120.2 |
| C2A—C3A—C4A | 120.78 (16) | C2B—C3B—C4B | 121.15 (14) |
| C2A—C3A—H3AA | 119.6 | C2B—C3B—H3BA | 119.4 |
| C4A—C3A—H3AA | 119.6 | C4B—C3B—H3BA | 119.4 |
| C5A—C4A—C3A | 119.30 (15) | C5B—C4B—C3B | 119.05 (14) |
| C5A—C4A—H4AA | 120.4 | C5B—C4B—H4BA | 120.5 |
| C3A—C4A—H4AA | 120.4 | C3B—C4B—H4BA | 120.5 |
| C4A—C5A—C6A | 121.29 (16) | C4B—C5B—C6B | 121.54 (14) |
| C4A—C5A—H5AA | 119.4 | C4B—C5B—H5BA | 119.2 |
| C6A—C5A—H5AA | 119.4 | C6B—C5B—H5BA | 119.2 |
| C5A—C6A—C1A | 118.66 (14) | C5B—C6B—C1B | 118.36 (13) |
| C5A—C6A—C7A | 120.15 (14) | C5B—C6B—C7B | 121.13 (13) |

| | | | |
|---|---|---|---|
| C1A—C6A—C7A | 121.18 (12) | C1B—C6B—C7B | 120.50 (13) |
| O1A—C7A—O2A | 123.35 (14) | O1B—C7B—O2B | 123.09 (14) |
| O1A—C7A—C6A | 119.44 (12) | O1B—C7B—C6B | 119.41 (13) |
| O2A—C7A—C6A | 117.21 (13) | O2B—C7B—C6B | 117.49 (12) |
| C10A—N1A—C9A | 122.06 (14) | C9B—N1B—C10B | 121.76 (13) |
| C10A—N1A—H1NA | 118.1 (12) | C9B—N1B—H1NB | 117.6 (12) |
| C9A—N1A—H1NA | 119.8 (12) | C10B—N1B—H1NB | 120.6 (12) |
| C9A—N2A—H2NA | 119.0 (12) | C9B—N2B—H2NB | 120.4 (11) |
| C9A—N2A—H3NA | 118.2 (12) | C9B—N2B—H3NB | 119.0 (11) |
| H2NA—N2A—H3NA | 122.8 (17) | H2NB—N2B—H3NB | 119.2 (16) |
| C12A—C8A—C9A | 120.89 (15) | C12B—C8B—C9B | 120.48 (13) |
| C12A—C8A—H8AA | 119.6 | C12B—C8B—H8BA | 119.8 |
| C9A—C8A—H8AA | 119.6 | C9B—C8B—H8BA | 119.8 |
| N2A—C9A—N1A | 118.14 (14) | N2B—C9B—N1B | 117.99 (13) |
| N2A—C9A—C8A | 124.06 (15) | N2B—C9B—C8B | 123.61 (13) |
| N1A—C9A—C8A | 117.80 (14) | N1B—C9B—C8B | 118.39 (13) |
| C11A—C10A—N1A | 121.14 (15) | N1B—C10B—C11B | 121.03 (14) |
| C11A—C10A—H10A | 119.4 | N1B—C10B—H10B | 119.5 |
| N1A—C10A—H10A | 119.4 | C11B—C10B—H10B | 119.5 |
| C10A—C11A—C12A | 119.10 (15) | C10B—C11B—C12B | 119.38 (13) |
| C10A—C11A—H11A | 120.4 | C10B—C11B—H11B | 120.3 |
| C12A—C11A—H11A | 120.4 | C12B—C11B—H11B | 120.3 |
| C8A—C12A—C11A | 119.01 (15) | C8B—C12B—C11B | 118.95 (13) |
| C8A—C12A—C13A | 121.66 (16) | C8B—C12B—C13B | 121.20 (14) |
| C11A—C12A—C13A | 119.33 (15) | C11B—C12B—C13B | 119.84 (13) |
| C12A—C13A—H13A | 109.5 | C12B—C13B—H13D | 109.5 |
| C12A—C13A—H13B | 109.5 | C12B—C13B—H13E | 109.5 |
| H13A—C13A—H13B | 109.5 | H13D—C13B—H13E | 109.5 |
| C12A—C13A—H13C | 109.5 | C12B—C13B—H13F | 109.5 |
| H13A—C13A—H13C | 109.5 | H13D—C13B—H13F | 109.5 |
| H13B—C13A—H13C | 109.5 | H13E—C13B—H13F | 109.5 |
| | | | |
| O3A—C1A—C2A—C3A | 178.90 (15) | O3B—C1B—C2B—C3B | −179.74 (13) |
| C6A—C1A—C2A—C3A | −0.7 (2) | C6B—C1B—C2B—C3B | 0.2 (2) |
| C1A—C2A—C3A—C4A | 0.5 (3) | C1B—C2B—C3B—C4B | 0.0 (2) |
| C2A—C3A—C4A—C5A | 0.3 (3) | C2B—C3B—C4B—C5B | −0.3 (2) |
| C3A—C4A—C5A—C6A | −0.9 (3) | C3B—C4B—C5B—C6B | 0.4 (2) |
| C4A—C5A—C6A—C1A | 0.6 (2) | C4B—C5B—C6B—C1B | −0.1 (2) |
| C4A—C5A—C6A—C7A | −178.47 (15) | C4B—C5B—C6B—C7B | 179.23 (13) |
| O3A—C1A—C6A—C5A | −179.39 (14) | O3B—C1B—C6B—C5B | 179.82 (13) |
| C2A—C1A—C6A—C5A | 0.2 (2) | C2B—C1B—C6B—C5B | −0.1 (2) |
| O3A—C1A—C6A—C7A | −0.4 (2) | O3B—C1B—C6B—C7B | 0.4 (2) |
| C2A—C1A—C6A—C7A | 179.26 (14) | C2B—C1B—C6B—C7B | −179.52 (12) |
| C5A—C6A—C7A—O1A | −1.0 (2) | C5B—C6B—C7B—O1B | −0.6 (2) |
| C1A—C6A—C7A—O1A | −179.99 (14) | C1B—C6B—C7B—O1B | 178.75 (13) |
| C5A—C6A—C7A—O2A | 178.56 (14) | C5B—C6B—C7B—O2B | −179.89 (13) |
| C1A—C6A—C7A—O2A | −0.5 (2) | C1B—C6B—C7B—O2B | −0.52 (19) |
| C10A—N1A—C9A—N2A | 179.75 (14) | C10B—N1B—C9B—N2B | −179.26 (13) |

| | | | |
|---|---|---|---|
| C10A—N1A—C9A—C8A | −0.5 (2) | C10B—N1B—C9B—C8B | −0.3 (2) |
| C12A—C8A—C9A—N2A | 179.56 (14) | C12B—C8B—C9B—N2B | 179.36 (14) |
| C12A—C8A—C9A—N1A | −0.2 (2) | C12B—C8B—C9B—N1B | 0.4 (2) |
| C9A—N1A—C10A—C11A | 0.8 (2) | C9B—N1B—C10B—C11B | 0.7 (2) |
| N1A—C10A—C11A—C12A | −0.5 (2) | N1B—C10B—C11B—C12B | −1.2 (2) |
| C9A—C8A—C12A—C11A | 0.5 (2) | C9B—C8B—C12B—C11B | −0.9 (2) |
| C9A—C8A—C12A—C13A | −178.45 (14) | C9B—C8B—C12B—C13B | 177.87 (14) |
| C10A—C11A—C12A—C8A | −0.2 (2) | C10B—C11B—C12B—C8B | 1.3 (2) |
| C10A—C11A—C12A—C13A | 178.81 (14) | C10B—C11B—C12B—C13B | −177.53 (14) |

*Hydrogen-bond geometry (Å, °)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| O3A—H1A3···O2A | 0.99 (2) | 1.61 (2) | 2.5310 (16) | 154 (2) |
| N1A—H1NA···O1B[i] | 0.99 (2) | 1.71 (2) | 2.6965 (17) | 174 (2) |
| N2A—H2NA···O1A[ii] | 0.90 (2) | 1.99 (2) | 2.8645 (19) | 164 (2) |
| O3B—H1B3···O2B | 0.94 (3) | 1.62 (3) | 2.5179 (16) | 158 (2) |
| N2A—H3NA···O2B[i] | 0.94 (2) | 1.91 (2) | 2.8468 (18) | 178 (2) |
| N1B—H1NB···O2A | 0.96 (2) | 1.76 (2) | 2.7186 (17) | 172.7 (17) |
| N2B—H2NB···O1A | 0.96 (2) | 1.84 (2) | 2.7976 (18) | 177.0 (16) |
| N2B—H3NB···O1B[iii] | 0.93 (2) | 1.88 (2) | 2.8097 (19) | 174.3 (13) |
| C8B—H8BA···O2B[iv] | 0.93 | 2.47 | 3.357 (2) | 159 |
| C10B—H10B···O3B | 0.93 | 2.38 | 3.039 (2) | 128 |

Symmetry codes: (i) −x+1, −y+1, −z+1; (ii) x, y+1, z; (iii) x, y−1, z; (iv) −x, −y, −z+1.