

Pseudopolymorphs of chelidamic acid and its dimethyl ester

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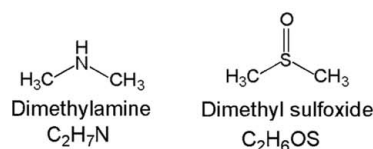
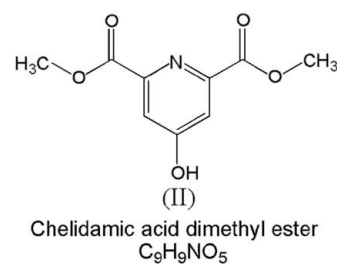
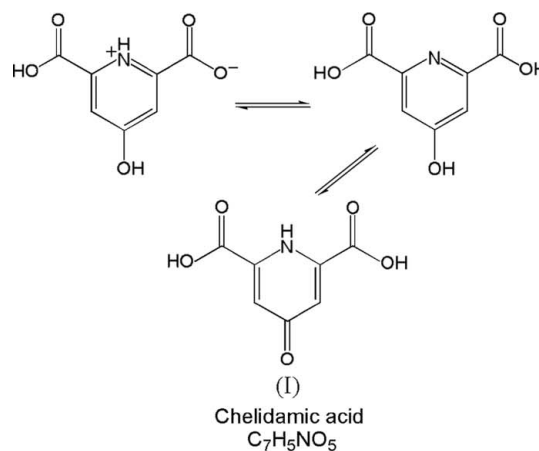
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Different tautomeric and zwitterionic forms of chelidamic acid (4-hydroxypyridine-2,6-dicarboxylic acid) are present in the crystal structures of chelidamic acid methanol monosolvate, $C_7H_5NO_5 \cdot CH_4O$, (*Ia*), dimethylammonium chelidamate (dimethylammonium 6-carboxy-4-hydroxypyridine-2-carboxylate), $C_2H_8N^+ \cdot C_7H_4NO_5^-$, (*Ib*), and chelidamic acid dimethyl sulfoxide monosolvate, $C_7H_5NO_5 \cdot C_2H_6OS$, (*Ic*). While the zwitterionic pyridinium carboxylate in (*Ia*) can be explained from the pK_a values, a (partially) deprotonated hydroxy group in the presence of a neutral carboxy group, as observed in (*Ib*) and (*Ic*), is unexpected. In (*Ib*), there are two formula units in the asymmetric unit with the chelidamic acid entities connected by a symmetric $O-H \cdots O$ hydrogen bond. Also, crystals of chelidamic acid dimethyl ester (dimethyl 4-hydroxypyridine-2,6-dicarboxylate) were obtained as a monohydrate, $C_9H_9NO_5 \cdot H_2O$, (*IIa*), and as a solvent-free modification, in which both ester molecules adopt the hydroxypyridine form. In (*IIa*), the solvent water molecule stabilizes the synperiplanar conformation of both carbonyl O atoms with respect to the pyridine N atom by two $O-H \cdots O$ hydrogen bonds, whereas an antiperiplanar arrangement is observed in the water-free structure. A database study and *ab initio* energy calculations help to compare the stabilities of the various ester conformations.

Comment

Chelidamic acid, (I), and its derivatives are widely used as starting materials for multichelating ligands in coordination chemistry, biochemistry and medicinal chemistry (Zou *et al.*, 2009). They can adopt different tautomeric and zwitterionic forms, resulting from intra- or intermolecular proton transfer. A search of the Cambridge Structural Database (CSD, Version 5.33 of November 2011, plus two updates; Allen, 2002) for 4-hydroxypyridine and 4-pyridone fragments yielded 68 structures, of which 36 exhibit the hydroxypyridine tautomer [mean $C-O = 1.34$ (2) Å] and 32 the pyridone form [mean $C-O = 1.268$ (14) Å]. According to a density functional theory (DFT) study, unsubstituted 4-hydroxypyridine is

more stable than 4-pyridone; however, the stabilities are reversed if two methyl ester groups are substituted at positions 2 and 6 (Alkorta & Elguero, 2001). In order to examine these interesting structural aspects, we recrystallized chelidamic acid from various solvents and obtained a methanol monosolvate, (*Ia*), a dimethylammonium salt, (*Ib*), and a dimethyl sulfoxide monosolvate, (*Ic*). For comparison, we also crystallized its dimethyl ester as a monohydrate, (*IIa*), and as a solvent-free modification, (II), of lower crystal quality (Tutughamiarso *et al.*, 2009).



- (*Ia*) Chelidamic acid \cdot CH_3OH
 (*Ib*) Chelidamate \cdot $(CH_3)_2NH_2^+$
 (*Ic*) Chelidamic acid \cdot $(CH_3)_2SO$
 (*IIa*) Chelidamic acid dimethyl ester \cdot H_2O

Pseudopolymorph (*Ia*) crystallized in the monoclinic space group $P2_1/n$, with one chelidamic acid and one methanol molecule in the asymmetric unit (Fig. 1). Proton transfer from one of the carboxy groups to the pyridine N atom has led to a zwitterionic form. The O atoms of the carboxylate group are displaced by 0.183 (2) and 0.326 (2) Å in opposite directions from the planar pyridine ring [$N1-C2-C21-O21 = 168.44$ (13) $^\circ$ and $N1-C2-C21-O22 = -12.50$ (19) $^\circ$]. The planes through the neutral carboxy group and the pyridine ring enclose a dihedral angle of 6.1 (2) $^\circ$, with the carbonyl O atom synperiplanar to the N atom [$N1-C6-C61-O61 = 5.00$ (19) $^\circ$]. Two chelidamic acid and two methanol molecules form a centrosymmetric dimer held together by six hydrogen

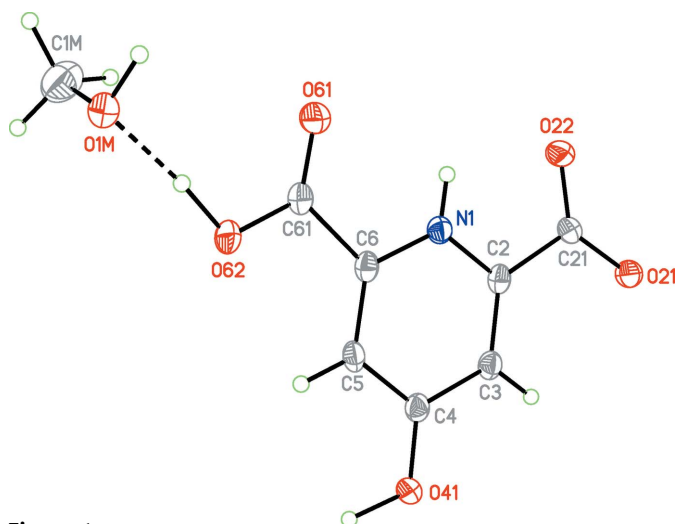


Figure 1
A perspective view of (*Ia*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line indicates an O—H...O hydrogen bond.

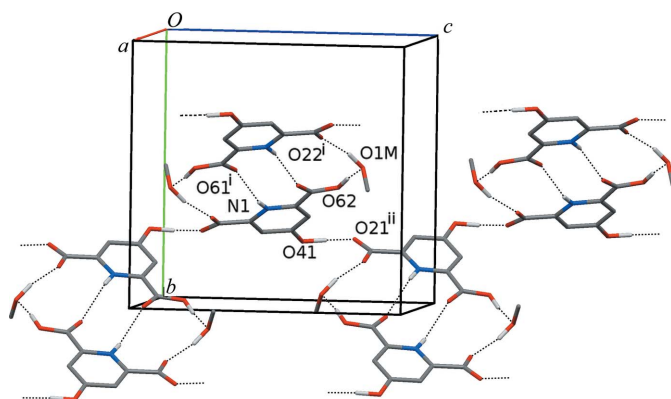


Figure 2
A partial packing diagram for (*Ia*). Dashed lines indicate hydrogen bonds. Only the H atoms involved in hydrogen bonding are shown. [Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$]

bonds: the chelidamic acid molecules are connected by an $R_2^2(10)$ interaction (Bernstein *et al.*, 1995) with two N—H...O hydrogen bonds and the chelidamic acid and the methanol molecules are connected by an $R_3^3(11)$ interaction with four O—H...O hydrogen bonds (Table 1 and Fig. 2). However, since the N1...O61 distance of 3.4354 (18) Å is well beyond the expected value for that kind of hydrogen bond, it seems that the two N—H...O interactions are more like close contacts resulting from the dimer formation through the O—H...O hydrogen bonds with the solvent. These dimers are linked into chains running along the *ac* diagonal by further O—H...O hydrogen bonds between the 4-hydroxy and carboxylate groups, with a dihedral angle of 65.21 (2)° between neighbouring chelidamic acid molecules.

Compound (*Ib*), which crystallized in the triclinic space group $P\bar{1}$, was obtained by recrystallization of chelidamic acid

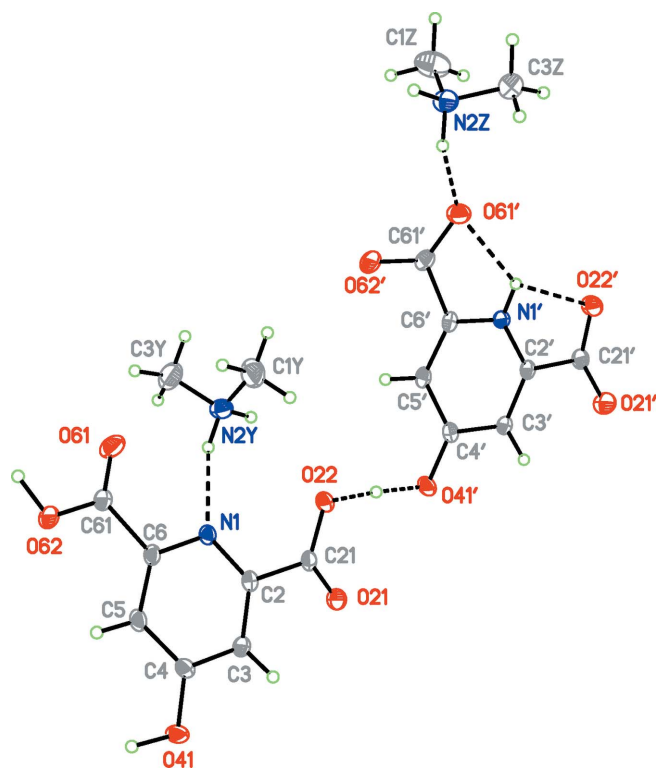


Figure 3
A perspective view of (*Ib*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed lines indicate hydrogen bonds and the two intramolecular N1'—H...O interactions.

from commercial dimethylformamide. Under the crystallization conditions, the solvent probably reacted with water to form formic acid and dimethylamine, which would explain the unexpected formation of the dimethylammonium salt of chelidamic acid. As another surprise, the asymmetric unit of (*Ib*) consists, apart from two dimethylammonium cations, either of one neutral acid molecule and one dianion or of two monoanions with different constitution, depending on the position of one H atom between the two chelidamic acid entities (Fig. 3). Actually carboxy atom O22 and hydroxy atom O41' are connected by a symmetric O—H...O hydrogen bond characterized by a very short O22...O41' distance of 2.4788 (15) Å, and O22—H22 and O41'—H22 distances of 1.24 (4) Å, which are significantly longer than a standard O—H bond. In the unprimed entity, the pyridine N atom is antiperiplanar to one of the carbonyl O atoms [N1—C2—C21—O21 = -157.69 (15)°] and synperiplanar to the other [N1—C6—C61—O61 = 7.9 (3)°]. In the primed entity, the planes of the carboxylate groups and the pyridine ring enclose dihedral angles of 4.9 (2) and 11.5 (2)°, respectively. The short distances between the N1'—H group and the carboxylate O atoms give rise to strong electrostatic interactions. Alternating chelidamic acid entities, whose planes enclose a dihedral angle of 17.45 (3)°, form double chains held together by two different $R_4^4(30)$ arrangements of O—H...O hydrogen bonds. The dimethylammonium cations connect these double chains

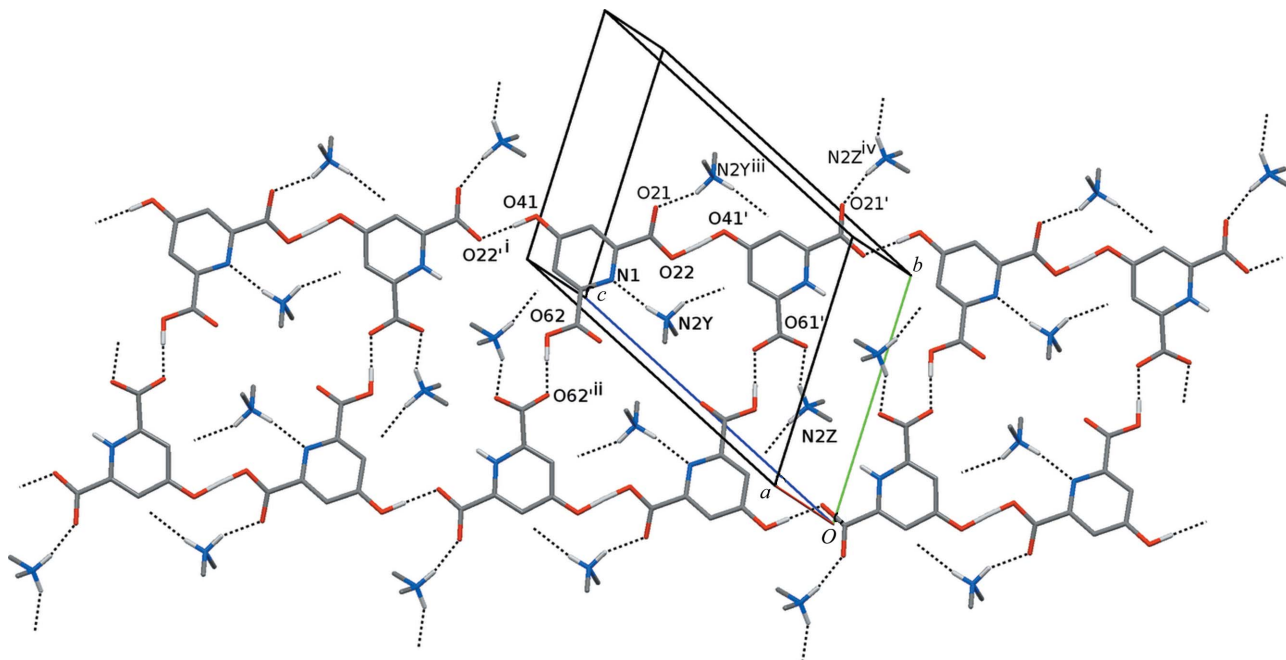


Figure 4

A partial packing diagram for (Ib). Dashed lines indicate hydrogen bonds. Only the H atoms involved in hydrogen bonding are shown. [Symmetry codes: (i) $x + 1, y - 1, z + 1$; (ii) $-x + 2, -y, -z + 1$; (iii) $-x + 2, -y + 1, -z + 1$; (iv) $x, y + 1, z$.]

into a three-dimensional network by N—H...N and N—H...O interactions (Table 2 and Fig. 4).

The asymmetric unit of pseudopolymorph (Ic), which also crystallized in $P\bar{1}$, contains one planar chelidamic acid (r.m.s. deviation = 0.022 Å for all non-H atoms) and one dimethyl sulfoxide molecule connected by an O—H...O hydrogen bond (Fig. 5). Both carbonyl O atoms are synperiplanar to the pyridine N atom [torsion angles = 3.46 (15) and -0.11 (15)°]. Since the latter is protonated, one would expect that, similar to (Ia), one of the carboxy groups is deprotonated. However, not

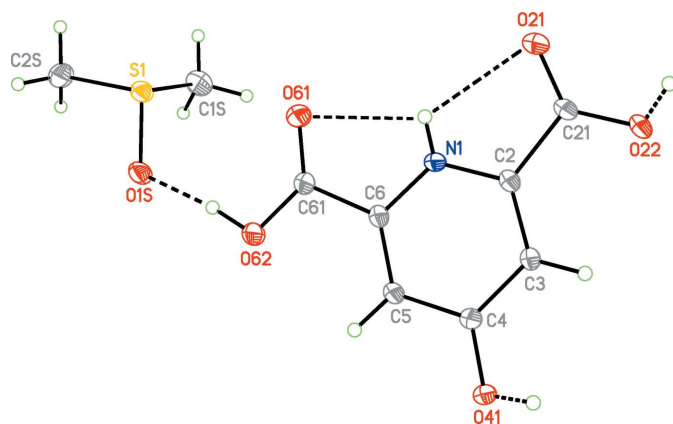


Figure 5

A perspective view of (Ic), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line between the two molecules indicates an O—H...O hydrogen bond, while the other four dashed lines show either intramolecular N—H...O interactions or bonds to H atoms disordered over two equally occupied positions.

only the H atom bonded to carboxy atom O22, but also that bonded to hydroxy atom O41, is disordered over two equally occupied positions on both sides of inversion centres. Thus, the molecular structure may be described as a superposition of four distinct forms: protonated and zwitterionic hydroxypyridine, as well as neutral and deprotonated pyridone. As in (Ib), there are close contacts between the protonated N atom and the neighbouring O atoms. The crystal packing of (Ic) shows layers parallel to the (111) plane held together by O—H...O and C—H...O interactions (the latter from atom C5 to the solvent molecule) (Table 3 and Fig. 6).

Compound (IIa) crystallized in the monoclinic space group $I2/a$ with one chelidamic acid dimethyl ester molecule and one water molecule in the asymmetric unit (Fig. 7). An $R_2^2(10)$ hydrogen-bonding pattern between the carbonyl O atoms and the water molecule stabilizes the synperiplanar conformation between these O atoms and the pyridine N atom [torsion angles = 0.2 (2) and 6.3 (2)°]. Furthermore, the water molecule accepts a hydrogen bond from the hydroxy group, thus forming chains along the a axis (Table 4 and Fig. 8). The conformation of (IIa) differs from that of the solvent-free structure of (II) (Fig. 9), where both carbonyl O atoms are antiperiplanar to the N atom (Tutughamiarso *et al.*, 2009).

In contrast to the DFT study (Alkorta & Elguero, 2001), chelidamic acid dimethyl ester adopts the hydroxypyridine tautomeric form in the solid state. However, the situation is more complex for (Ia)–(Ic). The pK_a values of chelidamic acid ($pK_{a1} = 1.4$, $pK_{a2} = 3.1$ and $pK_{a3} = 10.9$; Norkus *et al.*, 2003) suggest a proton transfer from one of the carboxy groups to the pyridine N atom. The zwitterionic form present in (Ia) is therefore expected; it is also observed in the crystal structure of chelidamic acid monohydrate (CSD refcode KIXCUP; Hall

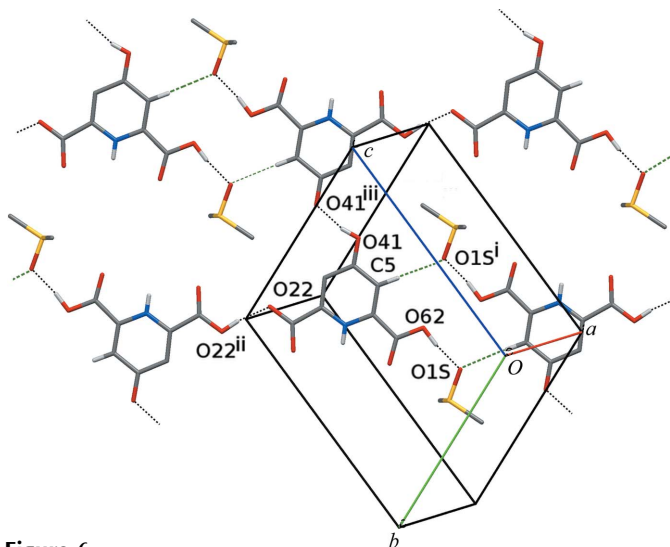


Figure 6
A partial packing diagram for (Ic). Dashed lines indicate hydrogen bonds. Only the H atoms involved in hydrogen bonding and only one site of each disordered H atom are shown. [Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x, -y + 2, -z + 2$; (iii) $-x + 1, -y + 1, -z + 2$.]

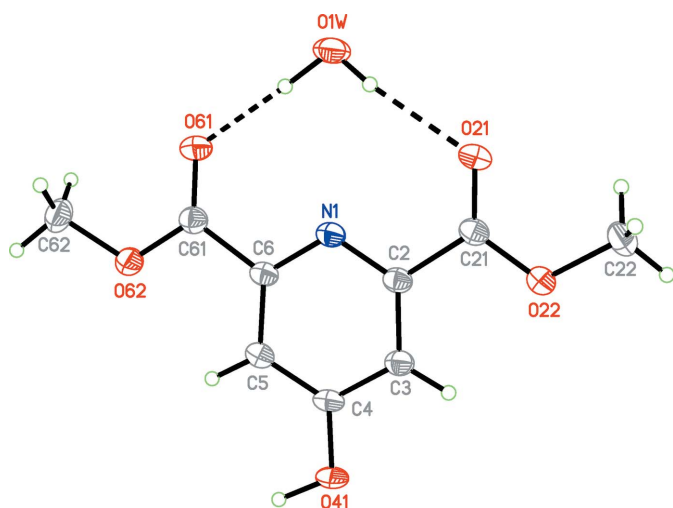


Figure 7
A perspective view of (IIa), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. Only the major occupied sites of the disordered methyl groups are shown.

et al., 2000), but with an antiperiplanar conformation between the carbonyl O and the pyridine N atom.

In the short O41'—H···O22 hydrogen bond observed in (Ib), the H atom is located very close to the mid-point between the two O atoms. Therefore it is not possible to clearly distinguish which group is deprotonated. A similar hydrogen bond is observed in the structure of the guanidinium salt of chelidamic acid [O···O and O—H distances = 2.46, 1.19 and 1.30 Å; refcode SARJIF (Moghimi *et al.*, 2005)]. A comparison of the C—O bond lengths in (Ib) with standard values (Allen *et al.*, 1987) and those in (Ia) shows that the substituent at atom C2 is rather close to a neutral carboxy group, while the C4'—O41' bond length of 1.2899 (18) Å resembles that of a

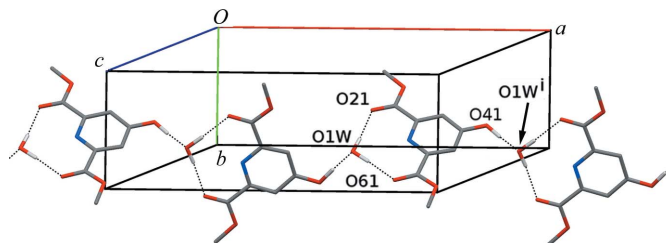


Figure 8
A partial packing diagram for (IIa). Dashed lines indicate hydrogen bonds. Only the H atoms involved in hydrogen bonding are shown. [Symmetry code: (i) $x + \frac{1}{2}, -y + 2, z$.]

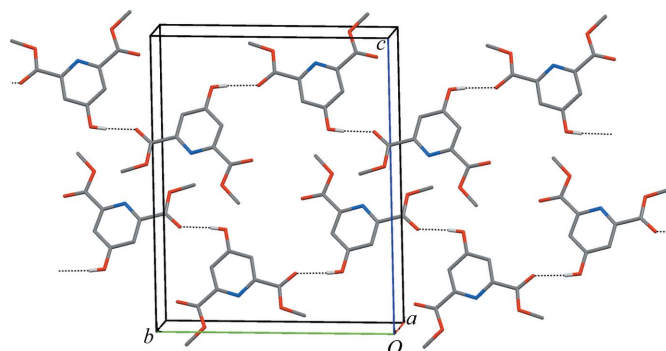


Figure 9
A partial packing diagram for the solvent-free structure of (II), showing hydrogen-bonded chains. Dashed lines indicate hydrogen bonds. Only the H atoms involved in hydrogen bonding are shown.

phenolate ion (Table 5). So it seems that this hydroxy group is at least partially deprotonated in the presence of a neutral carboxy group at C6.

That this is not pure speculation is confirmed by structure (Ic), which shows C—O bond lengths similar to those in (Ib). Here, clearly one H atom is shared between two carboxy groups and one between two hydroxy groups, again in the presence of a —COOH group at atom C6. In view of the pK_a values mentioned above, these are unexpected results. The O—H···O hydrogen bond connecting two hydroxy groups (of which one is deprotonated) may also be regarded as a connection between a protonated hydroxypyridine and a pyridone moiety (Fig. 6).

Although three of the four pyridine N atoms in (Ia)–(Ic) are protonated, there are no strong intermolecular N—H···O interactions resulting from that. In (Ia), there is only a rather long N—H···O hydrogen bond, whereas in (Ib) and (Ic), the N—H groups are not involved in the intermolecular hydrogen bonding. Instead they form close contacts (or perhaps intramolecular hydrogen bonds) to the neighbouring carboxylate and carboxy groups.

In (IIa) and the solvent-free form of (II), different conformations of the ester groups are observed. A CSD study of diesters of pyridine-2,6-dicarboxylic acids yielded 18 entries. Comparable with (IIa), ten entries show a synperiplanar (*sp*) conformation between both carbonyl O atoms and the pyridine N atom [refcodes ADEKOK (Huang & Xu, 2006), DELXUO (Gao *et al.*, 2006), EMOJAS (Felsmann *et al.*, 2011),

TIFQUU, TIFRAB, TIFREF, TIFRIJ, TIFROP, TIFRUV (Grossel *et al.*, 2001) and XEFDUH (Froidevaux *et al.*, 2000)]. In three entries, an antiperiplanar (*ap*) conformation similar to the solvent-free structure of (II) is observed [refcodes SAYXUM (Du *et al.*, 2006), VAHFOA (Habata *et al.*, 2001) and YIVYOC (Abhayawardhana *et al.*, 2007)]. In the remaining five entries, one carbonyl O atom adopts an *sp* and the other an *ap* conformation with respect to the pyridine N atom [refcodes DUZPIY (Kaboub *et al.*, 2010), GARROH (Bettencourt-Dias *et al.*, 2005), HOSPAG (Boger *et al.*, 1999), KITVOZ (Picot *et al.*, 2008) and XIBRUW (Santoni *et al.*, 2007)].

In order to compare the stabilities of the various conformers and tautomers of chelidamic acid dimethyl ester, (II), we have calculated the energies of the main conformers (*sp/sp*, *sp/ap* and *ap/ap*) of the hydroxypyridine and the pyridone tautomer by quantum-mechanical methods. For the hydroxypyridine tautomer, the *ap/ap* conformation [as in the solvent-free structure of (II)] is favoured by about 15 kJ mol⁻¹ compared to *sp/sp*. The opposite order resulted for the pyridone tautomer; here the *sp/sp* conformation is more stable than *ap/ap* by about 13 kJ mol⁻¹. For both series, the *sp/ap* energy is approximately the average of the other two. Obviously it makes a big difference for the preferred ester conformation if there is just an N atom or instead an N—H group between the COOR substituents. These calculations confirm that the *sp/sp* conformation observed in (IIa) is considerably stabilized by the bridging water molecule.

Experimental

Single crystals of (Ia), (Ib) and (Ic) were obtained by recrystallization of commercially available chelidamic acid from various solvents. Chelidamic acid (5.5 mg, 0.030 mmol) dissolved in methanol (520 µl) at 323 K yielded (Ia) by slow evaporation over several days. Salt (Ib) was obtained by recrystallization of chelidamic acid (5.1 mg, 0.028 mmol) from dimethylformamide (75 µl) at 323 K and pseudopolymorph (Ic) by recrystallization of chelidamic acid (5.1 mg, 0.028 mmol) from dimethyl sulfoxide (55 µl) at 269 K.

Chelidamic acid dimethyl ester was prepared from chelidamic acid (1.0 g, 0.005 mol) by reaction with methanol (75 ml) in the presence of sulfuric acid (100 µl). After refluxing at 373 K for 2 h, the mixture was cooled and extracted with ethyl acetate (3 × 185 ml) from water. The organic layer was dried over magnesium sulfate. The solvent was removed, whereupon (IIa) precipitated as a light-yellow solid (0.97 g, 84%). [The solvent-free form had been obtained by recrystallization of chelidamic acid dimethyl ester (5.5 mg, 0.026 mmol) from tetrahydrofuran (50 µl) at room temperature.]

Pseudopolymorph (Ia)

Crystal data

C ₇ H ₅ NO ₅ ·CH ₄ O	V = 917.96 (14) Å ³
M _r = 215.16	Z = 4
Monoclinic, P2 ₁ /n	Mo Kα radiation
a = 5.8256 (5) Å	μ = 0.14 mm ⁻¹
b = 12.5648 (12) Å	T = 173 K
c = 12.7464 (11) Å	0.52 × 0.50 × 0.44 mm
β = 100.303 (7)°	

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

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O61 ⁱ	0.86 (2)	2.61 (2)	3.4354 (18)	163.7 (19)
O41—H41...O21 ⁱⁱ	1.07 (3)	1.43 (3)	2.4827 (14)	170 (2)
O62—H62...O1M	1.03 (3)	1.50 (3)	2.5274 (15)	174 (3)
O1M—H1M...O22 ⁱ	0.97 (3)	1.71 (3)	2.6617 (16)	167 (2)

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

Data collection

Stoe IPDS II two-circle diffractometer
8713 measured reflections

1712 independent reflections
1491 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.096$
 $S = 1.07$
1712 reflections
153 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

Salt (Ib)

Crystal data

C₂H₈N⁺·C₇H₄NO₅⁻
M_r = 228.20
Triclinic, P $\bar{1}$
a = 7.3688 (8) Å
b = 11.1416 (12) Å
c = 14.3584 (15) Å
α = 69.025 (8)°
β = 79.438 (9)°

γ = 72.455 (9)°
V = 1045.74 (19) Å³
Z = 4
Mo Kα radiation
μ = 0.12 mm⁻¹
T = 173 K
0.42 × 0.40 × 0.40 mm

Data collection

Stoe IPDS II two-circle diffractometer
10298 measured reflections

3884 independent reflections
3102 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.066$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.114$
 $S = 1.00$
3884 reflections
325 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

Pseudopolymorph (Ic)

Crystal data

C₇H₅NO₅·C₂H₆OS
M_r = 261.25
Triclinic, P $\bar{1}$
a = 4.7460 (4) Å
b = 10.4917 (9) Å
c = 11.9787 (11) Å
α = 103.592 (7)°
β = 97.606 (7)°

γ = 101.651 (7)°
V = 557.59 (9) Å³
Z = 2
Mo Kα radiation
μ = 0.31 mm⁻¹
T = 173 K
0.36 × 0.28 × 0.22 mm

Data collection

Stoe IPDS II two-circle diffractometer
Absorption correction: multi-scan (MULABS; Spek, 2009; Blessing, 1995)
 $T_{\text{min}} = 0.897, T_{\text{max}} = 0.936$

11141 measured reflections
2552 independent reflections
2458 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$

Table 2

Hydrogen-bond geometry (Å, °) for (Ib).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O41'—H22...O22	1.24 (4)	1.24 (4)	2.4788 (15)	176 (3)
O41—H41...O22 ⁱⁱ	0.99 (3)	1.59 (3)	2.5765 (16)	175 (3)
O62—H62...O62 ⁱⁱⁱ	1.03 (3)	1.50 (3)	2.5255 (16)	174 (3)
N1'—H1'...O22'	0.87 (2)	2.31 (2)	2.6437 (17)	102.8 (15)
N1'—H1'...O61'	0.87 (2)	2.348 (19)	2.7095 (17)	105.0 (15)
N2Y—H2Y1...N1	0.92 (2)	2.13 (2)	3.005 (2)	159 (2)
N2Y—H2Y2...O21 ⁱⁱⁱ	0.96 (2)	1.94 (3)	2.8459 (19)	157.1 (19)
N2Z—H2Z2...O21 ^{iv}	0.96 (3)	1.82 (3)	2.7645 (19)	167 (2)
N2Z—H2Z1...O61'	0.96 (2)	1.93 (2)	2.8151 (19)	152.5 (18)

Symmetry codes: (i) $x + 1, y - 1, z + 1$; (ii) $-x + 2, -y, -z + 1$; (iii) $-x + 2, -y + 1, -z + 1$; (iv) $x, y - 1, z$.**Table 3**

Hydrogen-bond geometry (Å, °) for (Ic).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O21	0.818 (18)	2.289 (18)	2.6478 (12)	107.2 (14)
N1—H1...O61	0.818 (18)	2.331 (17)	2.6720 (12)	105.8 (14)
C5—H5...O1S ⁱ	0.95	2.31	3.2593 (13)	174
O22—H22...O22 ⁱⁱ	0.84	1.64	2.4703 (15)	170
O41—H41...O41 ⁱⁱⁱ	0.84	1.63	2.4509 (16)	166
O62—H62...O1S	0.94 (2)	1.61 (2)	2.5419 (12)	173 (2)

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.078$

$S = 1.06$

2552 reflections

169 parameters

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max} = 0.39 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.32 \text{ e } \text{Å}^{-3}$

Dimethyl ester (IIa)

Crystal data

 $\text{C}_9\text{H}_9\text{NO}_5 \cdot \text{H}_2\text{O}$ $M_r = 229.19$ Monoclinic, $I2/a$ $a = 17.241 (3) \text{ Å}$ $b = 6.1519 (12) \text{ Å}$ $c = 20.710 (4) \text{ Å}$ $\beta = 107.96 (3)^\circ$

$V = 2089.6 (7) \text{ Å}^3$

$Z = 8$

Mo $K\alpha$ radiation

$\mu = 0.12 \text{ mm}^{-1}$

 $T = 173 \text{ K}$ $0.40 \times 0.28 \times 0.13 \text{ mm}$

Data collection

Stoe IPDS II two-circle diffractometer

5752 measured reflections

1951 independent reflections

1474 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.080$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.100$

$S = 1.01$

1951 reflections

159 parameters

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max} = 0.17 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.23 \text{ e } \text{Å}^{-3}$

All H atoms were initially located by difference Fourier synthesis. Subsequently, H atoms bonded to C atoms were refined using a riding model, with methyl C—H = 0.98 Å and aromatic C—H = 0.95 Å, and

Table 4

Hydrogen-bond geometry (Å, °) for (IIa).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O41—H41...O1W ⁱ	1.00 (3)	1.62 (3)	2.6225 (19)	176 (2)
O1W—H1W...O61	0.99 (3)	1.88 (3)	2.869 (2)	176 (2)
O1W—H2W...O21	0.84 (3)	2.11 (3)	2.928 (2)	168 (2)

Symmetry code: (i) $x + \frac{1}{2}, -y + 2, z$.**Table 5**

C—O bond lengths (Å) for (Ia)–(Ic).

	(Ia)	(Ib)	(Ic)
C4—O41	1.3118 (18)	1.3410 (19)	1.2956 (13)
C4'—O41'		1.2899 (18)	
C21—O21	1.2644 (18)	1.2285 (19)	1.2317 (14)
C21'—O21'		1.246 (2)	
C21—O22	1.2409 (19)	1.2998 (18)	1.2823 (13)
C21'—O22'		1.2594 (19)	
C61—O61	1.2124 (19)	1.208 (2)	1.2180 (13)
C61'—O61'		1.246 (2)	
C61—O62	1.3136 (18)	1.318 (2)	1.3095 (13)
C61'—O62'		1.261 (2)	

with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl or $1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms. Apart from (IIa), the methyl groups were allowed to rotate about their local threefold axes.

In (Ia), (Ib) and (IIa), H atoms bonded to N or O atoms were refined isotropically.

In (Ib), a symmetric hydrogen bond was verified by close examination of the difference electron-density map, which clearly showed one maximum between two O atoms.

In (Ic), H atoms bonded to the N atom and to carboxy atom O62 were refined isotropically. A free isotropic refinement of the H atoms bonded to carboxy atom O22 and hydroxy atom O41 resulted in symmetric hydrogen bonds, with both H atoms at inversion centres. However, the difference electron-density map revealed that both H atoms are disordered over two positions. They were therefore refined isotropically with O—H = 0.84 Å and a site-occupation factor of 0.5, and were allowed to rotate about the C—O bond.

In (IIa), the H atoms of both methyl groups are disordered over two positions, with site-occupation factors of 0.61 (2) and 0.70 (2) for the major occupied orientations. Owing to the large β value of $118.86 (1)^\circ$ for the standard space group setting $C2/c$ and correlation coefficients larger than 0.5 for several U_{13}/U_{11} and U_{13}/U_{33} pairs, the nonstandard setting $I2/a$ was used.

Ab initio energy calculations were performed with geometry optimization using GAUSSIAN (Frisch *et al.*, 2004) at the B3LYP/6-31++G(d,p) level starting from the crystal structures and conformations derived thereof.

For all compounds, data collection: X-Area (Stoe & Cie, 2001); cell refinement: X-Area; data reduction: X-Area; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: Mercury (Macrae *et al.*, 2008) and XP (Sheldrick, 2008); software used to prepare material for publication: publCIF (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3095). Services for accessing these data are described at the back of the journal.

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supplementary materials

Acta Cryst. (2012). C68, o344–o350 [doi:10.1107/S0108270112031691]

Pseudopolymorphs of chelidamic acid and its dimethyl ester

Maya Tutughamiarso, Thorsten Pisternick and Ernst Egert

(Ia) 4-hydroxypyridine-2,6-dicarboxylic acid methanol monosolvate

Crystal data

$C_7H_5NO_5 \cdot CH_4O$

$M_r = 215.16$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 5.8256$ (5) Å

$b = 12.5648$ (12) Å

$c = 12.7464$ (11) Å

$\beta = 100.303$ (7)°

$V = 917.96$ (14) Å³

$Z = 4$

$F(000) = 448$

$D_x = 1.557$ Mg m⁻³

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

Cell parameters from 12422 reflections

$\theta = 3.2$ – 25.9 °

$\mu = 0.14$ mm⁻¹

$T = 173$ K

Block, yellow

$0.52 \times 0.50 \times 0.44$ mm

Data collection

Stoe IPDS II two-circle
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

8713 measured reflections

1712 independent reflections

1491 reflections with $I > 2\sigma(I)$

$R_{int} = 0.043$

$\theta_{max} = 25.6$ °, $\theta_{min} = 3.2$ °

$h = -5 \rightarrow 7$

$k = -15 \rightarrow 15$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.096$

$S = 1.07$

1712 reflections

153 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 0.3671P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.18$ e Å⁻³

$\Delta\rho_{min} = -0.26$ e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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	0.6359 (2)	0.63208 (10)	0.45800 (9)	0.0174 (3)
H1	0.760 (4)	0.6038 (17)	0.4439 (16)	0.037 (5)*
C2	0.4981 (2)	0.68738 (11)	0.37964 (11)	0.0170 (3)
C3	0.2995 (3)	0.73542 (11)	0.39842 (11)	0.0183 (3)
H3	0.2024	0.7731	0.3428	0.022*
C4	0.2381 (3)	0.72914 (11)	0.50048 (11)	0.0181 (3)
C5	0.3849 (3)	0.66925 (11)	0.58014 (11)	0.0182 (3)
H5	0.3469	0.6617	0.6492	0.022*
C6	0.5812 (3)	0.62263 (11)	0.55661 (11)	0.0171 (3)
C21	0.5859 (3)	0.69354 (11)	0.27464 (11)	0.0174 (3)
O21	0.44112 (19)	0.72881 (9)	0.19653 (8)	0.0246 (3)
O22	0.79039 (19)	0.66493 (9)	0.27627 (8)	0.0252 (3)
O41	0.04962 (18)	0.77874 (9)	0.51697 (8)	0.0219 (3)
H41	0.021 (5)	0.774 (2)	0.597 (2)	0.064 (7)*
C61	0.7573 (3)	0.56000 (11)	0.63437 (11)	0.0187 (3)
O61	0.9366 (2)	0.52961 (9)	0.60839 (8)	0.0266 (3)
O62	0.69101 (19)	0.54420 (9)	0.72637 (8)	0.0230 (3)
H62	0.825 (5)	0.505 (2)	0.775 (2)	0.065 (7)*
C1M	1.1971 (3)	0.52753 (15)	0.89663 (16)	0.0395 (5)
H1M1	1.1487	0.5720	0.9519	0.059*
H1M2	1.2307	0.5728	0.8386	0.059*
H1M3	1.3374	0.4875	0.9273	0.059*
O1M	1.0126 (2)	0.45452 (9)	0.85558 (9)	0.0273 (3)
H1M	1.077 (4)	0.403 (2)	0.8130 (19)	0.055 (7)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0171 (7)	0.0204 (6)	0.0148 (6)	-0.0007 (5)	0.0028 (5)	-0.0001 (5)
C2	0.0191 (7)	0.0175 (7)	0.0138 (7)	-0.0041 (5)	0.0009 (5)	-0.0003 (5)
C3	0.0192 (7)	0.0215 (7)	0.0138 (7)	-0.0011 (6)	0.0013 (6)	0.0016 (5)
C4	0.0176 (7)	0.0205 (7)	0.0157 (7)	-0.0039 (6)	0.0017 (6)	-0.0024 (5)
C5	0.0205 (7)	0.0226 (7)	0.0113 (6)	-0.0037 (6)	0.0028 (5)	-0.0008 (5)
C6	0.0189 (7)	0.0181 (7)	0.0137 (7)	-0.0045 (6)	0.0010 (5)	-0.0008 (5)
C21	0.0194 (7)	0.0185 (7)	0.0151 (7)	-0.0003 (5)	0.0049 (5)	-0.0004 (5)
O21	0.0230 (6)	0.0378 (6)	0.0138 (5)	0.0073 (5)	0.0052 (4)	0.0057 (4)
O22	0.0214 (6)	0.0361 (6)	0.0192 (5)	0.0071 (5)	0.0064 (4)	0.0016 (5)
O41	0.0189 (6)	0.0321 (6)	0.0153 (5)	0.0037 (4)	0.0046 (4)	-0.0001 (4)
C61	0.0211 (8)	0.0196 (7)	0.0147 (7)	-0.0025 (6)	0.0015 (6)	-0.0013 (5)
O61	0.0271 (6)	0.0336 (6)	0.0198 (6)	0.0080 (5)	0.0057 (5)	0.0031 (4)
O62	0.0239 (6)	0.0310 (6)	0.0138 (5)	0.0027 (5)	0.0025 (4)	0.0046 (4)
C1M	0.0359 (10)	0.0373 (10)	0.0412 (10)	0.0040 (8)	-0.0044 (8)	-0.0034 (8)

O1M 0.0280 (6) 0.0334 (6) 0.0197 (6) 0.0064 (5) 0.0020 (5) -0.0002 (5)

Geometric parameters (Å, °)

N1—C2	1.3556 (19)	C21—O22	1.2409 (19)
N1—C6	1.3559 (19)	C21—O21	1.2644 (18)
N1—H1	0.86 (2)	O41—H41	1.07 (3)
C2—C3	1.364 (2)	C61—O61	1.2124 (19)
C2—C21	1.5179 (19)	C61—O62	1.3136 (18)
C3—C4	1.412 (2)	O62—H62	1.03 (3)
C3—H3	0.9500	C1M—O1M	1.439 (2)
C4—O41	1.3118 (18)	C1M—H1M1	0.9800
C4—C5	1.421 (2)	C1M—H1M2	0.9800
C5—C6	1.365 (2)	C1M—H1M3	0.9800
C5—H5	0.9500	O1M—H1M	0.97 (3)
C6—C61	1.513 (2)		
C2—N1—C6	121.45 (13)	C5—C6—C61	125.13 (13)
C2—N1—H1	118.1 (14)	O22—C21—O21	128.17 (14)
C6—N1—H1	120.4 (14)	O22—C21—C2	116.38 (12)
N1—C2—C3	120.45 (13)	O21—C21—C2	115.45 (12)
N1—C2—C21	115.30 (13)	C4—O41—H41	114.1 (14)
C3—C2—C21	124.23 (13)	O61—C61—O62	126.96 (13)
C2—C3—C4	119.98 (13)	O61—C61—C6	120.06 (13)
C2—C3—H3	120.0	O62—C61—C6	112.98 (13)
C4—C3—H3	120.0	C61—O62—H62	107.2 (15)
O41—C4—C3	118.57 (13)	O1M—C1M—H1M1	109.5
O41—C4—C5	123.47 (13)	O1M—C1M—H1M2	109.5
C3—C4—C5	117.96 (14)	H1M1—C1M—H1M2	109.5
C6—C5—C4	119.42 (13)	O1M—C1M—H1M3	109.5
C6—C5—H5	120.3	H1M1—C1M—H1M3	109.5
C4—C5—H5	120.3	H1M2—C1M—H1M3	109.5
N1—C6—C5	120.72 (13)	C1M—O1M—H1M	107.0 (14)
N1—C6—C61	114.14 (13)		
C6—N1—C2—C3	0.1 (2)	C4—C5—C6—N1	-0.6 (2)
C6—N1—C2—C21	178.30 (12)	C4—C5—C6—C61	177.79 (13)
N1—C2—C3—C4	1.0 (2)	N1—C2—C21—O22	-12.50 (19)
C21—C2—C3—C4	-177.04 (13)	C3—C2—C21—O22	165.63 (14)
C2—C3—C4—O41	178.04 (13)	N1—C2—C21—O21	168.44 (13)
C2—C3—C4—C5	-1.9 (2)	C3—C2—C21—O21	-13.4 (2)
O41—C4—C5—C6	-178.22 (13)	N1—C6—C61—O61	5.00 (19)
C3—C4—C5—C6	1.7 (2)	C5—C6—C61—O61	-173.51 (14)
C2—N1—C6—C5	-0.3 (2)	N1—C6—C61—O62	-174.55 (12)
C2—N1—C6—C61	-178.86 (12)	C5—C6—C61—O62	6.9 (2)

Hydrogen-bond geometry (Å, °)

<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>
N1—H1 \cdots O61 ⁱ	0.86 (2)	2.61 (2)	3.4354 (18)	163.7 (19)

O41—H41···O21 ⁱⁱ	1.07 (3)	1.43 (3)	2.4827 (14)	170 (2)
O62—H62···O1M	1.03 (3)	1.50 (3)	2.5274 (15)	174 (3)
O1M—H1M···O22 ⁱ	0.97 (3)	1.71 (3)	2.6617 (16)	167 (2)

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

(Ib) dimethylammonium 6-carboxy-4-hydroxypyridine-2-carboxylate

Crystal data

$C_2H_8N^+ \cdot C_7H_4NO_5^-$	$Z = 4$
$M_r = 228.20$	$F(000) = 480$
Triclinic, $P\bar{1}$	$D_x = 1.449 \text{ Mg m}^{-3}$
Hall symbol: $-P 1$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 7.3688 (8) \text{ \AA}$	Cell parameters from 11295 reflections
$b = 11.1416 (12) \text{ \AA}$	$\theta = 3.0\text{--}25.7^\circ$
$c = 14.3584 (15) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$\alpha = 69.025 (8)^\circ$	$T = 173 \text{ K}$
$\beta = 79.438 (9)^\circ$	Block, colourless
$\gamma = 72.455 (9)^\circ$	$0.42 \times 0.40 \times 0.40 \text{ mm}$
$V = 1045.74 (19) \text{ \AA}^3$	

Data collection

Stoe IPDS II two-circle diffractometer	3102 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{\text{int}} = 0.066$
Graphite monochromator	$\theta_{\text{max}} = 25.5^\circ, \theta_{\text{min}} = 3.0^\circ$
ω scans	$h = -7 \rightarrow 8$
10298 measured reflections	$k = -13 \rightarrow 13$
3884 independent reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.043$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.114$	$w = 1/[\sigma^2(F_o^2) + (0.0746P)^2]$
$S = 1.00$	where $P = (F_o^2 + 2F_c^2)/3$
3884 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
325 parameters	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	1.07354 (19)	0.18057 (13)	0.69845 (10)	0.0147 (3)
C2	1.0139 (2)	0.28878 (15)	0.72811 (11)	0.0144 (3)
C3	1.0279 (2)	0.28679 (15)	0.82396 (12)	0.0175 (3)
H3	0.9845	0.3665	0.8407	0.021*
C4	1.1065 (2)	0.16621 (16)	0.89543 (12)	0.0176 (3)
C5	1.1719 (2)	0.05255 (15)	0.86574 (12)	0.0172 (3)
H5	1.2275	-0.0314	0.9115	0.021*
C6	1.1536 (2)	0.06554 (15)	0.76771 (12)	0.0153 (3)
C21	0.9266 (2)	0.42058 (15)	0.65175 (11)	0.0149 (3)
O21	0.92447 (18)	0.52509 (11)	0.66324 (9)	0.0219 (3)
O22	0.85769 (17)	0.41137 (11)	0.57818 (8)	0.0192 (3)
H22	0.767 (5)	0.522 (4)	0.526 (3)	0.098 (12)*
O41	1.1166 (2)	0.16544 (12)	0.98795 (9)	0.0270 (3)
H41	1.190 (5)	0.079 (3)	1.030 (2)	0.077 (9)*
C61	1.2267 (2)	-0.05173 (15)	0.72877 (12)	0.0190 (4)
O61	1.2311 (2)	-0.03798 (12)	0.64113 (10)	0.0376 (4)
O62	1.2869 (2)	-0.16665 (11)	0.79828 (9)	0.0253 (3)
H62	1.327 (5)	-0.242 (3)	0.767 (3)	0.089 (10)*
N1'	0.4435 (2)	0.69879 (13)	0.22462 (10)	0.0153 (3)
H1'	0.399 (3)	0.711 (2)	0.1687 (16)	0.024 (5)*
C2'	0.4312 (2)	0.80344 (15)	0.25502 (12)	0.0142 (3)
C3'	0.5037 (2)	0.78274 (15)	0.34220 (11)	0.0149 (3)
H3'	0.4905	0.8560	0.3643	0.018*
C4'	0.5991 (2)	0.65216 (15)	0.40032 (11)	0.0149 (3)
C5'	0.6102 (2)	0.54665 (15)	0.36362 (12)	0.0166 (3)
H5'	0.6732	0.4580	0.3995	0.020*
C6'	0.5312 (2)	0.57165 (15)	0.27748 (12)	0.0154 (3)
C21'	0.3387 (2)	0.94067 (15)	0.18491 (12)	0.0178 (3)
O21'	0.3214 (2)	1.03734 (11)	0.21314 (9)	0.0269 (3)
O22'	0.29196 (19)	0.93962 (11)	0.10517 (9)	0.0248 (3)
O41'	0.67307 (17)	0.63405 (11)	0.48060 (8)	0.0198 (3)
C61'	0.5305 (2)	0.46417 (15)	0.23593 (12)	0.0183 (3)
O61'	0.42720 (19)	0.49618 (11)	0.16680 (9)	0.0246 (3)
O62'	0.6373 (2)	0.35127 (12)	0.27677 (10)	0.0325 (3)
C1Y	0.9274 (3)	0.1873 (2)	0.47622 (18)	0.0404 (6)
H1Y1	0.9031	0.2087	0.4065	0.061*
H1Y2	0.8229	0.2415	0.5085	0.061*
H1Y3	0.9356	0.0929	0.5119	0.061*
N2Y	1.1090 (2)	0.21580 (14)	0.47896 (11)	0.0223 (3)
H2Y1	1.132 (3)	0.198 (2)	0.5439 (18)	0.032 (6)*
H2Y2	1.097 (3)	0.309 (2)	0.4466 (18)	0.039 (6)*
C3Y	1.2769 (3)	0.14836 (19)	0.42541 (15)	0.0360 (5)
H3Y1	1.3070	0.0523	0.4605	0.054*
H3Y2	1.3866	0.1820	0.4232	0.054*
H3Y3	1.2482	0.1661	0.3570	0.054*
C1Z	0.3843 (4)	0.3340 (2)	0.02766 (15)	0.0401 (5)
H1Z1	0.3347	0.2929	-0.0088	0.060*

H1Z2	0.5226	0.2964	0.0300	0.060*
H1Z3	0.3573	0.4302	-0.0065	0.060*
N2Z	0.2908 (2)	0.30742 (14)	0.13127 (11)	0.0243 (3)
H2Z1	0.344 (3)	0.350 (2)	0.1637 (16)	0.031 (5)*
H2Z2	0.317 (4)	0.213 (3)	0.1651 (18)	0.046 (7)*
C3Z	0.0795 (3)	0.3568 (2)	0.13578 (17)	0.0358 (5)
H3Z1	0.0439	0.4517	0.0971	0.054*
H3Z2	0.0280	0.3440	0.2056	0.054*
H3Z3	0.0271	0.3074	0.1077	0.054*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0160 (7)	0.0110 (6)	0.0150 (6)	-0.0018 (5)	-0.0034 (5)	-0.0019 (5)
C2	0.0124 (8)	0.0122 (7)	0.0162 (8)	-0.0020 (6)	-0.0018 (6)	-0.0025 (6)
C3	0.0215 (9)	0.0108 (7)	0.0183 (8)	-0.0002 (6)	-0.0044 (6)	-0.0044 (6)
C4	0.0205 (9)	0.0160 (8)	0.0148 (8)	-0.0026 (7)	-0.0053 (6)	-0.0033 (6)
C5	0.0190 (8)	0.0109 (7)	0.0187 (8)	-0.0010 (6)	-0.0062 (6)	-0.0013 (6)
C6	0.0159 (8)	0.0105 (7)	0.0176 (8)	-0.0012 (6)	-0.0033 (6)	-0.0032 (6)
C21	0.0124 (8)	0.0142 (8)	0.0132 (8)	0.0004 (6)	-0.0004 (6)	-0.0020 (6)
O21	0.0306 (7)	0.0117 (5)	0.0200 (6)	-0.0009 (5)	-0.0080 (5)	-0.0022 (4)
O22	0.0221 (6)	0.0151 (5)	0.0177 (6)	-0.0003 (5)	-0.0078 (5)	-0.0028 (5)
O41	0.0472 (9)	0.0154 (6)	0.0159 (6)	0.0019 (6)	-0.0138 (6)	-0.0050 (5)
C61	0.0225 (9)	0.0132 (8)	0.0189 (8)	0.0002 (7)	-0.0051 (7)	-0.0048 (6)
O61	0.0678 (11)	0.0175 (6)	0.0208 (7)	0.0062 (7)	-0.0122 (7)	-0.0085 (5)
O62	0.0413 (8)	0.0095 (5)	0.0215 (6)	0.0017 (5)	-0.0105 (6)	-0.0038 (5)
N1'	0.0173 (7)	0.0126 (6)	0.0149 (7)	-0.0012 (5)	-0.0041 (5)	-0.0040 (5)
C2'	0.0135 (8)	0.0103 (7)	0.0164 (8)	-0.0013 (6)	-0.0016 (6)	-0.0028 (6)
C3'	0.0147 (8)	0.0118 (7)	0.0170 (8)	-0.0008 (6)	-0.0019 (6)	-0.0050 (6)
C4'	0.0119 (8)	0.0145 (7)	0.0153 (7)	-0.0020 (6)	-0.0015 (6)	-0.0024 (6)
C5'	0.0170 (8)	0.0102 (7)	0.0192 (8)	0.0003 (6)	-0.0030 (6)	-0.0031 (6)
C6'	0.0130 (8)	0.0121 (7)	0.0187 (8)	-0.0009 (6)	-0.0006 (6)	-0.0046 (6)
C21'	0.0195 (9)	0.0121 (7)	0.0182 (8)	-0.0009 (6)	-0.0044 (7)	-0.0018 (6)
O21'	0.0407 (8)	0.0109 (5)	0.0264 (7)	-0.0010 (5)	-0.0112 (6)	-0.0036 (5)
O22'	0.0339 (8)	0.0168 (6)	0.0204 (6)	-0.0006 (5)	-0.0122 (5)	-0.0022 (5)
O41'	0.0243 (7)	0.0145 (5)	0.0181 (6)	-0.0004 (5)	-0.0103 (5)	-0.0022 (4)
C61'	0.0222 (9)	0.0131 (8)	0.0186 (8)	-0.0035 (7)	0.0000 (7)	-0.0056 (6)
O61'	0.0325 (7)	0.0203 (6)	0.0238 (6)	-0.0067 (5)	-0.0082 (5)	-0.0076 (5)
O62'	0.0446 (9)	0.0146 (6)	0.0384 (8)	0.0071 (6)	-0.0193 (6)	-0.0134 (5)
C1Y	0.0389 (13)	0.0246 (10)	0.0634 (15)	-0.0008 (9)	-0.0247 (11)	-0.0168 (10)
N2Y	0.0335 (9)	0.0168 (7)	0.0170 (7)	-0.0069 (6)	-0.0052 (6)	-0.0040 (6)
C3Y	0.0445 (13)	0.0268 (10)	0.0291 (10)	0.0023 (9)	0.0001 (9)	-0.0110 (8)
C1Z	0.0496 (14)	0.0513 (13)	0.0254 (10)	-0.0269 (11)	-0.0006 (9)	-0.0091 (9)
N2Z	0.0344 (9)	0.0157 (7)	0.0226 (8)	-0.0072 (7)	-0.0075 (7)	-0.0029 (6)
C3Z	0.0334 (11)	0.0332 (10)	0.0451 (12)	0.0010 (9)	-0.0112 (9)	-0.0218 (9)

Geometric parameters (\AA , $^\circ$)

N1—C2	1.344 (2)	C5'—H5'	0.9500
N1—C6	1.351 (2)	C6'—C61'	1.519 (2)

C2—C3	1.391 (2)	C21'—O21'	1.246 (2)
C2—C21	1.520 (2)	C21'—O22'	1.2594 (19)
C3—C4	1.398 (2)	O41'—H22	1.24 (4)
C3—H3	0.9500	C61'—O61'	1.246 (2)
C4—O41	1.3410 (19)	C61'—O62'	1.261 (2)
C4—C5	1.400 (2)	C1Y—N2Y	1.475 (3)
C5—C6	1.390 (2)	C1Y—H1Y1	0.9800
C5—H5	0.9500	C1Y—H1Y2	0.9800
C6—C61	1.516 (2)	C1Y—H1Y3	0.9800
C21—O21	1.2285 (19)	N2Y—C3Y	1.480 (3)
C21—O22	1.2998 (18)	N2Y—H2Y1	0.92 (2)
O22—H22	1.24 (4)	N2Y—H2Y2	0.96 (2)
O41—H41	0.99 (3)	C3Y—H3Y1	0.9800
C61—O61	1.208 (2)	C3Y—H3Y2	0.9800
C61—O62	1.318 (2)	C3Y—H3Y3	0.9800
O62—H62	1.03 (3)	C1Z—N2Z	1.486 (3)
N1'—C2'	1.3580 (19)	C1Z—H1Z1	0.9800
N1'—C6'	1.363 (2)	C1Z—H1Z2	0.9800
N1'—H1'	0.87 (2)	C1Z—H1Z3	0.9800
C2'—C3'	1.368 (2)	N2Z—C3Z	1.484 (3)
C2'—C21'	1.529 (2)	N2Z—H2Z1	0.96 (2)
C3'—C4'	1.427 (2)	N2Z—H2Z2	0.96 (3)
C3'—H3'	0.9500	C3Z—H3Z1	0.9800
C4'—O41'	1.2899 (18)	C3Z—H3Z2	0.9800
C4'—C5'	1.427 (2)	C3Z—H3Z3	0.9800
C5'—C6'	1.366 (2)		
C2—N1—C6	116.01 (13)	O21'—C21'—O22'	128.95 (14)
N1—C2—C3	123.88 (14)	O21'—C21'—C2'	116.58 (13)
N1—C2—C21	117.60 (13)	O22'—C21'—C2'	114.46 (13)
C3—C2—C21	118.52 (13)	C4'—O41'—H22	119.5 (15)
C2—C3—C4	119.30 (14)	O61'—C61'—O62'	127.66 (14)
C2—C3—H3	120.4	O61'—C61'—C6'	117.61 (14)
C4—C3—H3	120.4	O62'—C61'—C6'	114.73 (14)
O41—C4—C3	118.66 (14)	N2Y—C1Y—H1Y1	109.5
O41—C4—C5	123.58 (14)	N2Y—C1Y—H1Y2	109.5
C3—C4—C5	117.76 (14)	H1Y1—C1Y—H1Y2	109.5
C6—C5—C4	118.42 (14)	N2Y—C1Y—H1Y3	109.5
C6—C5—H5	120.8	H1Y1—C1Y—H1Y3	109.5
C4—C5—H5	120.8	H1Y2—C1Y—H1Y3	109.5
N1—C6—C5	124.59 (14)	C1Y—N2Y—C3Y	115.05 (16)
N1—C6—C61	113.74 (13)	C1Y—N2Y—H2Y1	110.2 (14)
C5—C6—C61	121.66 (14)	C3Y—N2Y—H2Y1	110.8 (14)
O21—C21—O22	125.28 (14)	C1Y—N2Y—H2Y2	108.8 (14)
O21—C21—C2	119.51 (13)	C3Y—N2Y—H2Y2	105.5 (15)
O22—C21—C2	115.21 (13)	H2Y1—N2Y—H2Y2	106.0 (18)
C21—O22—H22	111.5 (15)	N2Y—C3Y—H3Y1	109.5
C4—O41—H41	112.8 (18)	N2Y—C3Y—H3Y2	109.5
O61—C61—O62	124.21 (14)	H3Y1—C3Y—H3Y2	109.5

O61—C61—C6	121.75 (14)	N2Y—C3Y—H3Y3	109.5
O62—C61—C6	114.03 (13)	H3Y1—C3Y—H3Y3	109.5
C61—O62—H62	109.8 (19)	H3Y2—C3Y—H3Y3	109.5
C2'—N1'—C6'	121.91 (13)	N2Z—C1Z—H1Z1	109.5
C2'—N1'—H1'	120.8 (13)	N2Z—C1Z—H1Z2	109.5
C6'—N1'—H1'	117.2 (13)	H1Z1—C1Z—H1Z2	109.5
N1'—C2'—C3'	120.11 (14)	N2Z—C1Z—H1Z3	109.5
N1'—C2'—C21'	115.84 (13)	H1Z1—C1Z—H1Z3	109.5
C3'—C2'—C21'	124.03 (13)	H1Z2—C1Z—H1Z3	109.5
C2'—C3'—C4'	120.64 (13)	C3Z—N2Z—C1Z	113.65 (16)
C2'—C3'—H3'	119.7	C3Z—N2Z—H2Z1	110.5 (13)
C4'—C3'—H3'	119.7	C1Z—N2Z—H2Z1	106.3 (13)
O41'—C4'—C5'	123.14 (14)	C3Z—N2Z—H2Z2	105.7 (15)
O41'—C4'—C3'	120.28 (13)	C1Z—N2Z—H2Z2	109.8 (15)
C5'—C4'—C3'	116.57 (13)	H2Z1—N2Z—H2Z2	111.0 (19)
C6'—C5'—C4'	120.72 (14)	N2Z—C3Z—H3Z1	109.5
C6'—C5'—H5'	119.6	N2Z—C3Z—H3Z2	109.5
C4'—C5'—H5'	119.6	H3Z1—C3Z—H3Z2	109.5
N1'—C6'—C5'	120.01 (13)	N2Z—C3Z—H3Z3	109.5
N1'—C6'—C61'	116.22 (13)	H3Z1—C3Z—H3Z3	109.5
C5'—C6'—C61'	123.75 (14)	H3Z2—C3Z—H3Z3	109.5
C6—N1—C2—C3	-1.1 (2)	C6'—N1'—C2'—C3'	-1.6 (2)
C6—N1—C2—C21	178.83 (13)	C6'—N1'—C2'—C21'	176.68 (14)
N1—C2—C3—C4	-0.6 (3)	N1'—C2'—C3'—C4'	2.3 (2)
C21—C2—C3—C4	179.49 (15)	C21'—C2'—C3'—C4'	-175.86 (15)
C2—C3—C4—O41	-179.07 (15)	C2'—C3'—C4'—O41'	177.55 (15)
C2—C3—C4—C5	1.4 (3)	C2'—C3'—C4'—C5'	-1.3 (2)
O41—C4—C5—C6	179.93 (16)	O41'—C4'—C5'—C6'	-179.23 (15)
C3—C4—C5—C6	-0.6 (2)	C3'—C4'—C5'—C6'	-0.5 (2)
C2—N1—C6—C5	2.0 (2)	C2'—N1'—C6'—C5'	-0.1 (2)
C2—N1—C6—C61	-177.23 (14)	C2'—N1'—C6'—C61'	178.70 (15)
C4—C5—C6—N1	-1.2 (3)	C4'—C5'—C6'—N1'	1.1 (3)
C4—C5—C6—C61	177.98 (16)	C4'—C5'—C6'—C61'	-177.57 (15)
N1—C2—C21—O21	-157.69 (15)	N1'—C2'—C21'—O21'	178.02 (15)
C3—C2—C21—O21	22.2 (2)	C3'—C2'—C21'—O21'	-3.7 (3)
N1—C2—C21—O22	22.7 (2)	N1'—C2'—C21'—O22'	-2.7 (2)
C3—C2—C21—O22	-157.35 (15)	C3'—C2'—C21'—O22'	175.56 (16)
N1—C6—C61—O61	7.9 (3)	N1'—C6'—C61'—O61'	-10.6 (2)
C5—C6—C61—O61	-171.34 (18)	C5'—C6'—C61'—O61'	168.19 (16)
N1—C6—C61—O62	-173.35 (14)	N1'—C6'—C61'—O62'	169.38 (15)
C5—C6—C61—O62	7.4 (2)	C5'—C6'—C61'—O62'	-11.9 (2)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O41'—H22...O22	1.24 (4)	1.24 (4)	2.4788 (15)	176 (3)
O41—H41...O22 ⁱⁱ	0.99 (3)	1.59 (3)	2.5765 (16)	175 (3)
O62—H62...O62 ⁱⁱⁱ	1.03 (3)	1.50 (3)	2.5255 (16)	174 (3)

N1'—H1'...O22'	0.87 (2)	2.31 (2)	2.6437 (17)	102.8 (15)
N1'—H1'...O61'	0.87 (2)	2.348 (19)	2.7095 (17)	105.0 (15)
N2Y—H2Y1...N1	0.92 (2)	2.13 (2)	3.005 (2)	159 (2)
N2Y—H2Y2...O21 ⁱⁱⁱ	0.96 (2)	1.94 (3)	2.8459 (19)	157.1 (19)
N2Z—H2Z2...O21 ^{iv}	0.96 (3)	1.82 (3)	2.7645 (19)	167 (2)
N2Z—H2Z1...O61'	0.96 (2)	1.93 (2)	2.8151 (19)	152.5 (18)

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

(Ic) 4-hydroxypyridine-2,6-dicarboxylic acid dimethyl sulfoxide monosolvate

Crystal data

$C_7H_5NO_5 \cdot C_2H_6OS$

$M_r = 261.25$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 4.7460$ (4) Å

$b = 10.4917$ (9) Å

$c = 11.9787$ (11) Å

$\alpha = 103.592$ (7)°

$\beta = 97.606$ (7)°

$\gamma = 101.651$ (7)°

$V = 557.59$ (9) Å³

$Z = 2$

$F(000) = 272$

$D_x = 1.556$ Mg m⁻³

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

Cell parameters from 17750 reflections

$\theta = 3.6$ – 27.9 °

$\mu = 0.31$ mm⁻¹

$T = 173$ K

Plate, colourless

$0.36 \times 0.28 \times 0.22$ mm

Data collection

Stoe IPDS II two-circle
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan

(*MULABS*; Spek, 2009; Blessing, 1995)

$T_{\min} = 0.897$, $T_{\max} = 0.936$

11141 measured reflections

2552 independent reflections

2458 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 27.6$ °, $\theta_{\min} = 3.6$ °

$h = -6 \rightarrow 6$

$k = -13 \rightarrow 13$

$l = -15 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.078$

$S = 1.06$

2552 reflections

169 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.1667P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.39$ e Å⁻³

$\Delta\rho_{\min} = -0.32$ e Å⁻³

Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.086 (9)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1	0.4687 (2)	0.78021 (9)	0.73731 (8)	0.01689 (19)	
H1	0.441 (4)	0.8353 (18)	0.7014 (15)	0.035 (4)*	
C2	0.3755 (2)	0.78845 (10)	0.84006 (9)	0.0164 (2)	
C3	0.4164 (2)	0.69729 (11)	0.90262 (9)	0.0183 (2)	
H3	0.3517	0.7037	0.9750	0.022*	
C4	0.5572 (2)	0.59265 (11)	0.85821 (9)	0.0184 (2)	
C5	0.6547 (2)	0.58953 (11)	0.74974 (9)	0.0181 (2)	
H5	0.7520	0.5226	0.7180	0.022*	
C6	0.6069 (2)	0.68340 (10)	0.69208 (9)	0.0164 (2)	
C21	0.2199 (2)	0.90220 (11)	0.87362 (10)	0.0190 (2)	
O21	0.1828 (2)	0.96876 (10)	0.80321 (8)	0.0312 (2)	
O22	0.13897 (19)	0.91346 (8)	0.97273 (7)	0.0247 (2)	
H22	0.0514	0.9760	0.9851	0.051 (11)*	0.50
O41	0.5992 (2)	0.50148 (9)	0.91080 (7)	0.0270 (2)	
H41	0.5245	0.5119	0.9711	0.042 (10)*	0.50
C61	0.6967 (2)	0.69305 (11)	0.57736 (9)	0.0184 (2)	
O61	0.6429 (2)	0.78174 (9)	0.53434 (7)	0.0273 (2)	
O62	0.8340 (2)	0.60150 (9)	0.53520 (7)	0.0277 (2)	
H62	0.875 (5)	0.617 (2)	0.464 (2)	0.068 (7)*	
S1	0.90608 (6)	0.74888 (3)	0.29997 (2)	0.01996 (11)	
O1S	0.9724 (2)	0.62973 (8)	0.34301 (7)	0.0256 (2)	
C1S	1.1706 (3)	0.89513 (12)	0.39007 (11)	0.0305 (3)	
H1S1	1.1381	0.9111	0.4708	0.046*	
H1S2	1.1513	0.9736	0.3613	0.046*	
H1S3	1.3679	0.8810	0.3876	0.046*	
C2S	1.0555 (3)	0.73813 (13)	0.16945 (11)	0.0277 (3)	
H2S1	1.2636	0.7390	0.1870	0.042*	
H2S2	1.0342	0.8154	0.1393	0.042*	
H2S3	0.9507	0.6541	0.1106	0.042*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0229 (4)	0.0171 (4)	0.0166 (4)	0.0107 (3)	0.0078 (3)	0.0088 (3)
C2	0.0185 (5)	0.0169 (5)	0.0171 (5)	0.0087 (4)	0.0067 (4)	0.0049 (4)
C3	0.0245 (5)	0.0199 (5)	0.0164 (5)	0.0118 (4)	0.0102 (4)	0.0074 (4)
C4	0.0249 (5)	0.0183 (5)	0.0177 (5)	0.0112 (4)	0.0084 (4)	0.0080 (4)
C5	0.0248 (5)	0.0173 (5)	0.0175 (5)	0.0112 (4)	0.0095 (4)	0.0064 (4)
C6	0.0200 (5)	0.0168 (5)	0.0152 (5)	0.0080 (4)	0.0072 (4)	0.0048 (4)
C21	0.0226 (5)	0.0190 (5)	0.0210 (5)	0.0126 (4)	0.0082 (4)	0.0075 (4)
O21	0.0480 (5)	0.0346 (5)	0.0279 (4)	0.0302 (4)	0.0172 (4)	0.0179 (4)
O22	0.0349 (4)	0.0263 (4)	0.0256 (4)	0.0216 (3)	0.0179 (3)	0.0122 (3)

O41	0.0472 (5)	0.0268 (4)	0.0227 (4)	0.0247 (4)	0.0194 (4)	0.0160 (3)
C61	0.0249 (5)	0.0184 (5)	0.0158 (5)	0.0088 (4)	0.0081 (4)	0.0065 (4)
O61	0.0443 (5)	0.0267 (4)	0.0227 (4)	0.0197 (4)	0.0158 (4)	0.0144 (3)
O62	0.0459 (5)	0.0299 (4)	0.0233 (4)	0.0250 (4)	0.0224 (4)	0.0153 (3)
S1	0.02493 (16)	0.02090 (16)	0.02033 (16)	0.01183 (11)	0.01011 (10)	0.00898 (11)
O1S	0.0436 (5)	0.0200 (4)	0.0240 (4)	0.0165 (3)	0.0195 (4)	0.0118 (3)
C1S	0.0409 (7)	0.0210 (5)	0.0299 (6)	0.0101 (5)	0.0060 (5)	0.0056 (5)
C2S	0.0393 (7)	0.0315 (6)	0.0221 (5)	0.0164 (5)	0.0149 (5)	0.0143 (5)

Geometric parameters (Å, °)

N1—C2	1.3519 (13)	O22—H22	0.8400
N1—C6	1.3638 (13)	O41—H41	0.8400
N1—H1	0.818 (18)	C61—O61	1.2180 (13)
C2—C3	1.3739 (14)	C61—O62	1.3095 (13)
C2—C21	1.5298 (14)	O62—H62	0.94 (2)
C3—C4	1.4319 (14)	S1—O1S	1.5318 (8)
C3—H3	0.9500	S1—C1S	1.7834 (13)
C4—O41	1.2956 (13)	S1—C2S	1.7898 (12)
C4—C5	1.4314 (14)	C1S—H1S1	0.9800
C5—C6	1.3662 (14)	C1S—H1S2	0.9800
C5—H5	0.9500	C1S—H1S3	0.9800
C6—C61	1.5110 (14)	C2S—H2S1	0.9800
C21—O21	1.2317 (14)	C2S—H2S2	0.9800
C21—O22	1.2823 (13)	C2S—H2S3	0.9800
C2—N1—C6	122.14 (9)	C21—O22—H22	109.5
C2—N1—H1	118.7 (12)	C4—O41—H41	109.5
C6—N1—H1	119.2 (12)	O61—C61—O62	126.58 (10)
N1—C2—C3	120.35 (9)	O61—C61—C6	119.79 (9)
N1—C2—C21	113.80 (9)	O62—C61—C6	113.62 (9)
C3—C2—C21	125.82 (9)	C61—O62—H62	105.7 (14)
C2—C3—C4	119.69 (9)	O1S—S1—C1S	105.86 (6)
C2—C3—H3	120.2	O1S—S1—C2S	104.46 (5)
C4—C3—H3	120.2	C1S—S1—C2S	97.38 (6)
O41—C4—C5	118.88 (9)	S1—C1S—H1S1	109.5
O41—C4—C3	123.46 (9)	S1—C1S—H1S2	109.5
C5—C4—C3	117.65 (9)	H1S1—C1S—H1S2	109.5
C6—C5—C4	119.59 (9)	S1—C1S—H1S3	109.5
C6—C5—H5	120.2	H1S1—C1S—H1S3	109.5
C4—C5—H5	120.2	H1S2—C1S—H1S3	109.5
N1—C6—C5	120.56 (9)	S1—C2S—H2S1	109.5
N1—C6—C61	113.75 (9)	S1—C2S—H2S2	109.5
C5—C6—C61	125.69 (9)	H2S1—C2S—H2S2	109.5
O21—C21—O22	128.33 (10)	S1—C2S—H2S3	109.5
O21—C21—C2	117.44 (10)	H2S1—C2S—H2S3	109.5
O22—C21—C2	114.21 (9)	H2S2—C2S—H2S3	109.5
C6—N1—C2—C3	-0.42 (16)	C4—C5—C6—N1	0.34 (16)
C6—N1—C2—C21	-178.69 (9)	C4—C5—C6—C61	179.97 (10)

N1—C2—C3—C4	-0.36 (16)	N1—C2—C21—O21	3.46 (15)
C21—C2—C3—C4	177.69 (10)	C3—C2—C21—O21	-174.70 (11)
C2—C3—C4—O41	-178.73 (10)	N1—C2—C21—O22	-177.90 (9)
C2—C3—C4—C5	1.07 (16)	C3—C2—C21—O22	3.94 (16)
O41—C4—C5—C6	178.75 (10)	N1—C6—C61—O61	-0.11 (15)
C3—C4—C5—C6	-1.06 (16)	C5—C6—C61—O61	-179.77 (11)
C2—N1—C6—C5	0.43 (16)	N1—C6—C61—O62	178.82 (9)
C2—N1—C6—C61	-179.24 (9)	C5—C6—C61—O62	-0.83 (16)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O21	0.818 (18)	2.289 (18)	2.6478 (12)	107.2 (14)
N1—H1...O61	0.818 (18)	2.331 (17)	2.6720 (12)	105.8 (14)
C5—H5...O1S ⁱ	0.95	2.31	3.2593 (13)	174
O22—H22...O22 ⁱⁱ	0.84	1.64	2.4703 (15)	170
O41—H41...O41 ⁱⁱⁱ	0.84	1.63	2.4509 (16)	166
O62—H62...O1S	0.94 (2)	1.61 (2)	2.5419 (12)	173 (2)

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

(IIa) dimethyl 4-hydroxypyridine-2,6-dicarboxylate monohydrate

Crystal data

C₉H₉NO₅·H₂O

M_r = 229.19

Monoclinic, *I*2/a

Hall symbol: -I 2ya

a = 17.241 (3) Å

b = 6.1519 (12) Å

c = 20.710 (4) Å

β = 107.96 (3)°

V = 2089.6 (7) Å³

Z = 8

F(000) = 960

D_x = 1.457 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 4497 reflections

θ = 3.5–25.8°

μ = 0.12 mm⁻¹

T = 173 K

Plate, colourless

0.40 × 0.28 × 0.13 mm

Data collection

Stoe IPDS II two-circle diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

5752 measured reflections

1951 independent reflections

1474 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.080

θ_{max} = 25.7°, θ_{min} = 3.5°

h = -18→20

k = -7→7

l = -25→25

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.039

wR(*F*²) = 0.100

S = 1.01

1951 reflections

159 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1	0.61782 (8)	0.8964 (2)	0.11852 (7)	0.0208 (3)	
C2	0.65285 (10)	0.7200 (3)	0.15439 (8)	0.0202 (4)	
C3	0.73477 (10)	0.6671 (3)	0.16862 (8)	0.0218 (4)	
H3	0.7565	0.5417	0.1947	0.026*	
C4	0.78472 (10)	0.8015 (3)	0.14384 (8)	0.0212 (4)	
C5	0.74899 (10)	0.9820 (3)	0.10443 (8)	0.0220 (4)	
H5	0.7801	1.0747	0.0853	0.026*	
C6	0.66635 (10)	1.0211 (3)	0.09425 (8)	0.0194 (4)	
C21	0.59473 (10)	0.5840 (3)	0.17920 (8)	0.0204 (4)	
C22	0.58219 (12)	0.2723 (3)	0.24261 (10)	0.0309 (4)	
H22A	0.5452	0.3622	0.2590	0.046*	0.61 (2)
H22B	0.6174	0.1873	0.2804	0.046*	0.61 (2)
H22C	0.5503	0.1736	0.2072	0.046*	0.61 (2)
H22D	0.5917	0.1198	0.2336	0.046*	0.39 (2)
H22E	0.5245	0.3079	0.2213	0.046*	0.39 (2)
H22F	0.5966	0.2954	0.2917	0.046*	0.39 (2)
O21	0.52335 (7)	0.6269 (2)	0.16812 (6)	0.0277 (3)	
O22	0.63235 (7)	0.41172 (19)	0.21477 (6)	0.0260 (3)	
O41	0.86443 (7)	0.7511 (2)	0.15935 (6)	0.0272 (3)	
H41	0.8940 (18)	0.849 (4)	0.1359 (14)	0.063 (8)*	
C61	0.62268 (11)	1.2146 (3)	0.05374 (8)	0.0217 (4)	
C62	0.63320 (13)	1.5086 (3)	-0.01640 (10)	0.0333 (4)	
H62A	0.5876	1.4572	-0.0546	0.050*	0.70 (2)
H62B	0.6735	1.5805	-0.0337	0.050*	0.70 (2)
H62C	0.6130	1.6120	0.0106	0.050*	0.70 (2)
H62D	0.6323	1.4821	-0.0633	0.050*	0.30 (2)
H62E	0.6646	1.6408	0.0007	0.050*	0.30 (2)
H62F	0.5773	1.5268	-0.0150	0.050*	0.30 (2)
O61	0.55315 (8)	1.2644 (2)	0.04852 (7)	0.0320 (3)	
O62	0.67108 (8)	1.32419 (19)	0.02594 (6)	0.0272 (3)	
O1W	0.44055 (8)	1.0083 (2)	0.09349 (7)	0.0314 (3)	
H1W	0.4801 (18)	1.090 (5)	0.0769 (14)	0.065 (8)*	
H2W	0.4657 (17)	0.895 (4)	0.1095 (13)	0.052 (8)*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0174 (7)	0.0252 (7)	0.0196 (7)	0.0014 (6)	0.0052 (6)	-0.0018 (6)
C2	0.0194 (9)	0.0236 (8)	0.0178 (8)	0.0010 (7)	0.0061 (6)	-0.0032 (7)
C3	0.0193 (8)	0.0254 (8)	0.0205 (9)	0.0028 (7)	0.0057 (7)	-0.0004 (7)
C4	0.0160 (8)	0.0270 (8)	0.0207 (9)	0.0024 (7)	0.0056 (6)	-0.0045 (7)
C5	0.0190 (9)	0.0246 (8)	0.0227 (9)	-0.0012 (7)	0.0069 (7)	-0.0013 (7)
C6	0.0168 (8)	0.0227 (8)	0.0185 (8)	0.0002 (6)	0.0053 (6)	-0.0030 (6)
C21	0.0201 (9)	0.0230 (8)	0.0189 (8)	-0.0007 (7)	0.0070 (7)	-0.0041 (7)
C22	0.0267 (10)	0.0337 (9)	0.0336 (10)	-0.0053 (8)	0.0113 (8)	0.0060 (8)
O21	0.0187 (6)	0.0340 (7)	0.0322 (7)	0.0020 (5)	0.0106 (5)	0.0031 (5)
O22	0.0215 (6)	0.0264 (6)	0.0313 (7)	0.0007 (5)	0.0099 (5)	0.0054 (5)
O41	0.0122 (6)	0.0345 (7)	0.0340 (7)	0.0038 (5)	0.0060 (5)	0.0033 (6)
C61	0.0208 (9)	0.0238 (8)	0.0198 (8)	0.0007 (7)	0.0053 (7)	-0.0017 (7)
C62	0.0334 (10)	0.0302 (9)	0.0329 (10)	0.0013 (8)	0.0052 (8)	0.0118 (8)
O61	0.0242 (7)	0.0347 (7)	0.0401 (8)	0.0104 (6)	0.0141 (6)	0.0094 (6)
O62	0.0217 (6)	0.0282 (6)	0.0304 (7)	0.0007 (5)	0.0062 (5)	0.0078 (5)
O1W	0.0192 (7)	0.0365 (7)	0.0394 (8)	0.0039 (6)	0.0103 (6)	-0.0002 (6)

Geometric parameters (\AA , $^\circ$)

N1—C6	1.342 (2)	C22—H22C	0.9800
N1—C2	1.348 (2)	C22—H22D	0.9800
C2—C3	1.390 (2)	C22—H22E	0.9800
C2—C21	1.512 (2)	C22—H22F	0.9800
C3—C4	1.401 (2)	O41—H41	1.00 (3)
C3—H3	0.9500	C61—O61	1.209 (2)
C4—O41	1.348 (2)	C61—O62	1.333 (2)
C4—C5	1.403 (2)	C62—O62	1.459 (2)
C5—C6	1.395 (2)	C62—H62A	0.9800
C5—H5	0.9500	C62—H62B	0.9800
C6—C61	1.516 (2)	C62—H62C	0.9800
C21—O21	1.210 (2)	C62—H62D	0.9800
C21—O22	1.339 (2)	C62—H62E	0.9800
C22—O22	1.457 (2)	C62—H62F	0.9800
C22—H22A	0.9800	O1W—H1W	0.99 (3)
C22—H22B	0.9800	O1W—H2W	0.84 (3)
C6—N1—C2	116.20 (14)	O22—C22—H22F	109.5
N1—C2—C3	123.98 (15)	H22A—C22—H22F	62.8
N1—C2—C21	113.67 (14)	H22B—C22—H22F	49.6
C3—C2—C21	122.35 (15)	H22C—C22—H22F	140.4
C2—C3—C4	118.91 (15)	H22D—C22—H22F	109.5
C2—C3—H3	120.5	H22E—C22—H22F	109.5
C4—C3—H3	120.5	C21—O22—C22	115.96 (14)
O41—C4—C3	118.28 (15)	C4—O41—H41	112.3 (16)
O41—C4—C5	123.61 (16)	O61—C61—O62	124.64 (15)
C3—C4—C5	118.11 (15)	O61—C61—C6	123.89 (16)
C6—C5—C4	117.98 (15)	O62—C61—C6	111.46 (14)

C6—C5—H5	121.0	O62—C62—H62A	109.5
C4—C5—H5	121.0	O62—C62—H62B	109.5
N1—C6—C5	124.77 (15)	H62A—C62—H62B	109.5
N1—C6—C61	113.31 (14)	O62—C62—H62C	109.5
C5—C6—C61	121.92 (15)	H62A—C62—H62C	109.5
O21—C21—O22	124.71 (16)	H62B—C62—H62C	109.5
O21—C21—C2	123.84 (15)	O62—C62—H62D	109.5
O22—C21—C2	111.45 (14)	H62A—C62—H62D	51.9
O22—C22—H22A	109.5	H62B—C62—H62D	60.6
O22—C22—H22B	109.5	H62C—C62—H62D	140.8
H22A—C22—H22B	109.5	O62—C62—H62E	109.5
O22—C22—H22C	109.5	H62A—C62—H62E	140.8
H22A—C22—H22C	109.5	H62B—C62—H62E	51.9
H22B—C22—H22C	109.5	H62C—C62—H62E	60.6
O22—C22—H22D	109.5	H62D—C62—H62E	109.5
H22A—C22—H22D	140.4	O62—C62—H62F	109.5
H22B—C22—H22D	62.8	H62A—C62—H62F	60.6
H22C—C22—H22D	49.6	H62B—C62—H62F	140.8
O22—C22—H22E	109.5	H62C—C62—H62F	51.9
H22A—C22—H22E	49.6	H62D—C62—H62F	109.5
H22B—C22—H22E	140.4	H62E—C62—H62F	109.5
H22C—C22—H22E	62.8	C61—O62—C62	115.39 (14)
H22D—C22—H22E	109.5	H1W—O1W—H2W	104 (2)
C6—N1—C2—C3	2.0 (2)	N1—C2—C21—O21	0.2 (2)
C6—N1—C2—C21	-178.91 (14)	C3—C2—C21—O21	179.35 (17)
N1—C2—C3—C4	-0.9 (3)	N1—C2—C21—O22	-179.68 (13)
C21—C2—C3—C4	-179.95 (15)	C3—C2—C21—O22	-0.5 (2)
C2—C3—C4—O41	178.48 (15)	O21—C21—O22—C22	-1.4 (2)
C2—C3—C4—C5	-1.3 (2)	C2—C21—O22—C22	178.48 (14)
O41—C4—C5—C6	-177.52 (15)	N1—C6—C61—O61	6.3 (2)
C3—C4—C5—C6	2.2 (2)	C5—C6—C61—O61	-173.56 (17)
C2—N1—C6—C5	-0.9 (2)	N1—C6—C61—O62	-174.92 (14)
C2—N1—C6—C61	179.27 (13)	C5—C6—C61—O62	5.2 (2)
C4—C5—C6—N1	-1.2 (2)	O61—C61—O62—C62	-3.6 (2)
C4—C5—C6—C61	178.65 (14)	C6—C61—O62—C62	177.62 (14)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O41—H41...O1W ⁱ	1.00 (3)	1.62 (3)	2.6225 (19)	176 (2)
O1W—H1W...O61	0.99 (3)	1.88 (3)	2.869 (2)	176 (2)
O1W—H2W...O21	0.84 (3)	2.11 (3)	2.928 (2)	168 (2)

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

Selected C—O bond lengths (Å)

	(Ia)	(Ib)	(Ic)
C4—O41	1.3118 (18)	1.3410 (19)	1.2956 (13)

C4'—O41'		1.2899 (18)	
C21—O21	1.2644 (18)	1.2285 (19)	1.2317 (14)
C21'—O21'		1.246 (2)	
C21—O22	1.2409 (19)	1.2998 (18)	1.2823 (13)
C21'—O22'		1.2594 (19)	
C61—O61	1.2124 (19)	1.208 (2)	1.2180 (13)
C61'—O61'		1.246 (2)	
C61—O62	1.3136 (18)	1.318 (2)	1.3095 (13)
C61'—O62'		1.261 (2)	
