N1—C7	1.365 (4)	C5—C6	1.376 (5)
N1—H5	0.88 (3)	C5—H3	0.91 (3)
N2—C7	1.367 (4)	C6—H4	0.91 (3)
N2—C8	1.402 (4)	C8—C9	1.391 (4)
N2—H6	0.93 (2)	C8—C12	1.387 (4)
N3—C9	1.340 (5)	C9—H7	1.03 (3)
N3—C10	1.334 (5)	C10—C11	1.380 (4)
C1—C2	1.370 (5)	C10—H8	1.09 (3)
C1—C6	1.378 (5)	C11—C12	1.373 (5)
C2—C3	1.374 (6)	C11—H9	1.11 (4)
C2—H1	1.00 (3)	C12—H10	0.95 (3)
C4—N1—C7	128.8 (2)	C1—C6—C5	119.7 (3)
C4—N1—H5	118 (2)	C1—C6—H4	119 (2)
C7—N1—H5	113 (2)	C5—C6—H4	121 (2)
C7—N2—C8	127.8 (2)	O—C7—N1	124.2 (3)
C7—N2—H6	118 (2)	O—C7—N2	124.3 (3)
C8—N2—H6	114 (2)	N1—C7—N2	111.5 (2)
C9—N3—C10	119.2 (3)	N2—C8—C9	124.5 (3)
Cl—C1—C2	120.7 (3)	N2—C8—C12	118.4 (2)
Cl—C1—C6	119.4 (3)	C9—C8—C12	117.1 (3)
C2—C1—C6	119.9 (3)	N3—C9—C8	122.5 (3)
C1—C2—C3	120.8 (3)	N3—C9—H7	122 (2)
C1—C2—H1	114 (2)	C8—C9—H7	115 (2)
C3—C2—H1	125 (2)	N3—C10—C11	122.1 (3)
C2—C3—C4	120.4 (3)	N3—C10—H8	122 (2)
C2—C3—H2	122 (2)	C11—C10—H8	116 (2)
C4—C3—H2	117 (2)	C10—C11—C12	118.4 (3)
N1—C4—C3	124.5 (3)	C10—C11—H9	120 (2)
N1—C4—C5	117.7 (3)	C12—C11—H9	121 (2)
C3—C4—C5	117.7 (3)	C8—C12—C11	120.7 (3)
C4—C5—C6	121.5 (3)	C8—C12—H10	120 (2)
C4—C5—H3	117 (3)	C11—C12—H10	119 (2)
C6—C5—H3	121 (3)		

Table 6. *Selected geometric parameters* (Å, °) *for* (3)

Cl—C1	1.751 (2)	C3—C4	1.392 (3)
O—C7	1.214 (3)	C3—H2	0.91 (2)
N1—C4	1.410 (3)	C4—C5	1.394 (3)
N1—C7	1.363 (3)	C5—C6	1.380 (3)
N1—H5	0.94 (2)	C5—H3	0.92 (2)
N2—C7	1.382 (3)	C6—H4	0.96 (2)
N2—C8	1.386 (3)	C8—C9	1.382 (3)
N2—H6	0.87 (2)	C8—C12	1.397 (3)
N3—C10	1.345 (3)	C9—C10	1.380 (4)
N3—C11	1.336 (3)	C9—H7	0.94 (2)
C1—C2	1.372 (3)	C10—H8	0.97 (2)
C1—C6	1.379 (4)	C11—C12	1.368 (4)
C2—C3	1.383 (3)	C11—H9	1.00 (2)
C2—H1	0.92 (2)	C12—H10	0.96 (3)
C4—N1—C7	127.1 (2)	C1—C6—C5	119.6 (2)
C4—N1—H5	119 (2)	C1—C6—H4	122 (2)
C7—N1—H5	113 (2)	C5—C6—H4	119 (1)
C7—N2—C8	127.1 (2)	O—C7—N1	124.6 (2)
C7—N2—H6	116 (1)	O—C7—N2	123.7 (2)
C8—N2—H6	117 (1)	N1—C7—N2	111.6 (2)
C10—N3—C11	114.5 (2)	N2—C8—C9	124.6 (2)
Cl—C1—C2	119.6 (2)	N2—C8—C12	118.4 (2)
Cl—C1—C6	119.4 (2)	C9—C8—C12	117.0 (2)
C2—C1—C6	121.1 (6)	C8—C9—C10	118.5 (2)
C1—C2—c3	119.3 (2)	C8—C9—H7	124 (1)
C1—C2—H1	119 (1)	C10—C9—H7	118 (1)
C3—C2—H1	121 (1)	N3—C10—C9	125.6 (2)
C2—C3—C4	120.9 (2)	N3—C10—H8	116 (1)
C2—C3—H2	120 (1)	C9—C10—H8	118 (1)
C4—C3—H2	119 (1)	N3—C11—C12	124.6 (2)
N1—C4—C3	117.1 (2)	N3—C11—H9	115 (1)
N1—C4—C5	124.4 (2)	C12—C11—H9	121 (1)
C3—C4—C5	118.5 (2)	C8—C12—C11	119.8 (2)
C4—C5—C6	120.6 (2)	C8—C12—H10	120 (2)
C4—C5—H3	122 (1)	C11—C12—H10	120 (2)
C6—C5—H3	117 (1)		

The structure was solved by direct methods and successive difference Fourier syntheses. All of the H atoms were located by difference Fourier synthesis. Full-matrix least-squares anisotropic (β_{ij}) refinement was carried out for all atoms except the H atoms, which were refined isotropically. All calculations were performed on a MicroVAX 3100 using the *MolEN* programs (Fair, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1069). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-Carboxymethyl-3-hydroxy-2-methyl-4(1*H*)-pyridinone (Monoclinic Form 2)

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Abstract

The structure of a second monoclinic polymorph of 1-carboxymethyl-3-hydroxy-2-methyl-4-pyridinone (3-hydroxy-2-methyl-4-oxopyridine-1-acetic acid, $C_8H_9NO_4$) is reported. The molecule has a delocalized zwitterionic structure much like that reported for form 1 [Zhang, Rettig & Orvig (1992). *Can. J. Chem.* **70**, 763–770]. The structure contains a legitimate intermolecular C—H···O hydrogen bond [H···O = 2.18 (2), C···O = 3.155 (3) Å, C—H···O = 165 (2)°]. The two forms differ primarily in the details of the hydrogen bonding.

Comment

Tautomerism is one of the most important features of heterocyclic compounds. For 4-pyridinones there

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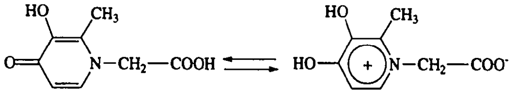
are two possible tautomers: 4-hydroxypyridine and 4-pyridinone (Elguero, Marzin, Katritzky & Linda, 1976). In the equilibrium between these two tautomers, the predominant form in polar solvents is the pyridinone; however, the hydroxypyridine tautomer appears to be the more stable of the two in the gas phase (Johnson, 1984; Gilchrist, 1985; Maqueatian, van Haverbeke, de Meyer, Katritzky, Cook & Page, 1975). The crystal structures of 3-hydroxy-2-methyl-4-pyridinone (Hmpp) and 3-hydroxy-1,2-dimethyl-4-pyridinone (Hdpp) (Nelson, Karpishin, Rettig & Orvig, 1988) show that these compounds exist as the pyridinone forms in the solid state and that the ring system of the pyridinones shows some delocalization of the formal double bonds. The effect of the ring N-atom substituent on the delocalization has also been discussed (Nelson, 1988). We have also determined the structures of 3-hydroxy-1-(*p*-methoxyphenyl)-2-methyl-4-pyridinone (Hpap) and 1-carboxymethyl-3-hydroxy-2-methyl-4-pyridinone (Hcmp) (Zhang, Rettig & Orvig, 1992). The pyridinone ring system in Hpap contains localized formal double bonds while this ring system in Hcmp appears to be delocalized, as a zwitterionic structure is formed (Zhang, Rettig & Orvig, 1992). Here we report the structure of a second crystalline form of Hcmp.



Hcmp

The geometry of the Hcmp molecule in this crystal form is very similar to that reported earlier for form 1 (Zhang, Rettig & Orvig, 1992), the largest differences between corresponding bond lengths being 0.008 (3) Å for C(5)—C(6) and 0.007 (3) Å for N(1)—C(6). [It should be noted that there are minor differences in the atom numbering: O(3), O(4), H(3), H(4), H(5), H(8) and H(9) in the present structure correspond to O(4), O(3), H(5), H(3), H(4), H(9) and H(8), respectively, in form 1.] The intramolecular bond angles in the two crystal forms exhibit some small (but statistically significant) differences. The plane of the carboxylate group is almost perpendicular to the plane of the aromatic ring, the angle between the normals to the mean planes being 83.9°, while the corresponding angle for form 1 is 91.0°.

In both crystal forms there are weak intramolecular O(1)—H···O(2) hydrogen bonds and weak intramolecular C(1)—H···O(1) interactions, the former interaction being weaker in form 2 than in form 1 [O···H = 2.29 (2) Å] while the latter interaction is virtually identical in the two polymorphs. The importance of weak C—H···O interactions in the determination of molecular conformation and in lattice stabilization, even when the geometry deviates from the classical 'ideal' hydrogen-bond values, has been recognized in a number of recent publications (*e.g.* Keller, Neeland, Rettig, Trotter & Weiler, 1988; Desiraju & Nalini, 1991; Wiborg, Waldron, Schulte & Saunders, 1991). The differences between the C(8)—O bonds [0.047 (3) Å in form 2; 0.039 (2) Å in form 1] are consistent with an overall structure derived predominantly from the zwitterionic form with a large contribution from the pyridinone form. This average structure is facilitated by the formation of a strong O(2)—H(2)···O(carboxylate) hydrogen bond (see below) and is further supported by the detailed molecular geometry.

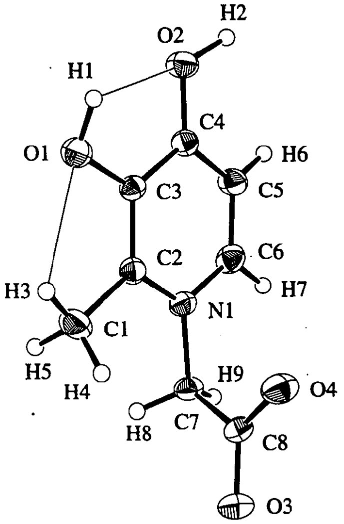


Fig. 1. Perspective view of 1-carboxymethyl-3-hydroxy-2-methyl-4-pyridinone; 33% probability displacement ellipsoids are shown for the non-H atoms. Fine lines represent hydrogen bonds or weak C—H···O interactions.

The intermolecular hydrogen bonding in the two crystal forms of Hcmp is shown in Fig. 2. The hydrogen-bonding schemes have several features in common. In both polymorphs the two OH-group H atoms are involved in intermolecular O—H···O hydrogen bonds, while the aromatic H atom adjacent to the ring N atom and a methylene H atom attached to C(7) are involved in C—H···O interactions, giving rise to a total of eight intermolecular interactions per molecule. The carboxylate O atoms O(3) and O(4) act as the only acceptors in the intermolecular interactions. Both polymorphs feature very strong O(2)—H(2)···O(carboxylate) hydrogen bonds that link the molecules head-to-tail to form infinite chains. These chains are further linked by the remaining intermolecular interactions to form three-dimensional networks. Examination of Fig. 2 reveals several differences between the hydrogen-bonding schemes. Each molecule in form 1 is linked to five different neighboring molecules by O—H···O hydrogen bonds and C—H···O interactions, while the molecules in form 2 are each linked to eight neighboring molecules. In form 1, both carboxylate O atoms [O(3) and O(4)] are involved in one O—H···O hydrogen bond and one weak C—H···O interaction, whereas in form 2, O(3) is only involved in O—H···O hydrogen bonding and O(4) is exclusively involved in C—H···O interactions. The involvement of O(3) in a second relatively strong O—H···O hydrogen bond in form 2 accounts for the weakening of the O(2)—H(2)···O(3) interaction relative to that in form 1 [O···O = 2.545 (2) *versus* 2.475 (1) Å]. This distinction between the carboxylate O atoms in the two polymorphs is also consistent with the larger difference between the two C(8)—O bond lengths in the present structure [0.047 (3) *versus* 0.039 (2) Å for form 1; the differences between the corresponding C(8)—O distances in the two forms are both 0.004 (2) Å, which is possibly significant]. The hydrogen bonding in form 1 results in centrosymmetric dimeric units linked *via* O(1)—H(1)···O(3) hydrogen bonds that are absent in form 2. Different C(7) methylene H atoms are involved in the C—H···O interactions in the two crystal forms: that directed towards C(6) in form 1 and that directed towards C(2) in form 2. The C(6)—H(7)···O(4) interaction in form 2 is considerably stronger than either C—H···O interaction in form 1 and may be classified as a legitimate C—H···O hydrogen bond. It is noteworthy that, despite an apparent advantage in intermolecular hydrogen bonding, the density of form 2 is lower than that of form 1 (1.487 *versus* 1.540 Mg m^{-3}), indicative of stronger overall van der Waals interactions in form 1. This may result from the fact that in form 1 each molecule is double-linked to three different molecules by pairs of either O—H···O hydrogen bonds or C—H···O interactions.

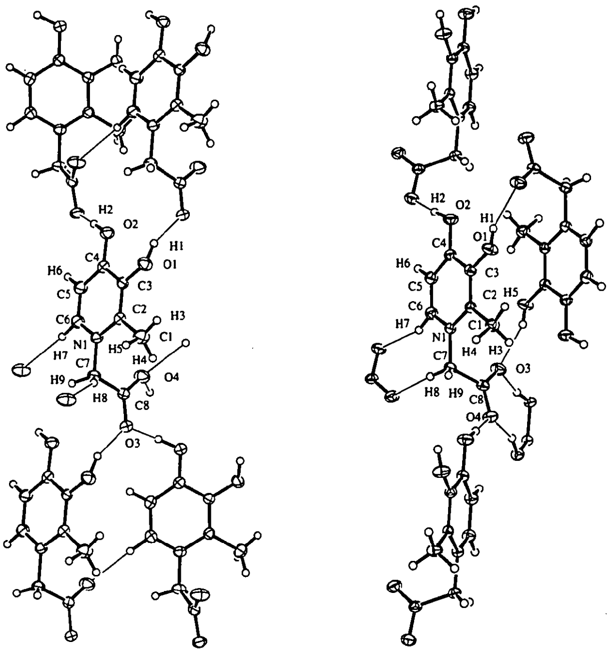


Fig. 2. Hydrogen bonding in the two polymorphs of 1-carboxymethyl-3-hydroxy-2-methyl-4-pyridinone (form 2 is on the left and form 1 is on the right). Fine lines represent intermolecular hydrogen bonds or C—H···O interactions. Other complete molecules shown are those linked to the labeled base molecule by O—H···O hydrogen bonding. For the sake of clarity, only those atoms (or moieties) directly involved in C—H···O interactions with the base molecule are shown.

Experimental

The title compound was prepared as decribed by Zhang, Rettig & Orvig (1992).

Crystal data

$C_8H_9NO_4$
M_r = 183.16
Monoclinic
$P2_1/c$
a = 8.380 (1) Å
b = 10.474 (4) Å
c = 9.554 (2) Å
β = 102.78 (1)°
V = 817.8 (3) Å^3
Z = 4
D_x = 1.487 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 18.9–21.9°
μ = 0.113 mm^{-1}
T = 294 K
Prism
0.45 × 0.24 × 0.15 mm
Colorless

Data collection

Rigaku AFC-6S diffractometer
ω-2θ scans
Absorption correction: empirical
$T_{\min}$ = 0.90, $T_{\max}$ = 1.00
2658 measured reflections
2380 independent reflections
1492 observed reflections [$I \geq 3\sigma(I)$]
$R_{\rm int}$ = 0.044

$\theta_{\max}$ = 30°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 14$
$l = -13 \rightarrow 13$
3 standard reflections monitored every 200 reflections
intensity variation: insignificant

Refinement

Refinement on F
R = 0.043
wR = 0.041
S = 2.85
1492 reflections
154 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max}$ = 0.02
$\Delta\rho_{\max}$ = 0.25 e Å^{-3}
$\Delta\rho_{\min}$ = −0.15 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$B_{\rm eq}$
O(1)	−0.0809 (2)	0.0315 (1)	0.2790 (1)	3.35 (6)
O(2)	−0.2241 (1)	0.1679 (1)	0.0406 (1)	3.31 (6)
O(3)	0.6775 (1)	0.1762 (1)	0.3353 (1)	3.33 (6)

O(4)	0.4438 (2)	0.2821 (1)	0.3122 (2)	4.20 (6)
N(1)	0.2688 (2)	0.1063 (1)	0.1354 (2)	2.59 (6)
C(1)	0.2554 (3)	−0.0105 (2)	0.3573 (3)	3.9 (1)
C(2)	0.1764 (2)	0.0612 (2)	0.2256 (2)	2.52 (7)
C(3)	0.0092 (2)	0.0823 (2)	0.1917 (2)	2.37 (6)
C(4)	−0.0639 (2)	0.1513 (2)	0.0681 (2)	2.61 (7)
C(5)	0.0364 (2)	0.1958 (2)	−0.0190 (2)	3.27 (8)
C(6)	0.1994 (2)	0.1722 (2)	0.0154 (2)	3.24 (8)
C(7)	0.4479 (2)	0.0942 (2)	0.1705 (2)	2.83 (7)
C(8)	0.5259 (2)	0.1937 (2)	0.2821 (2)	2.67 (7)

Table 2. *Selected geometric parameters* (Å, °)

O(1)—C(3)	1.352 (2)	C(1)—C(2)	1.489 (3)
O(2)—C(4)	1.321 (2)	C(2)—C(3)	1.384 (2)
O(3)—C(8)	1.273 (2)	C(3)—C(4)	1.404 (2)
O(4)—C(8)	1.226 (2)	C(4)—C(5)	1.387 (3)
N(1)—C(2)	1.364 (2)	C(5)—C(6)	1.355 (3)
N(1)—C(6)	1.355 (2)	C(7)—C(8)	1.529 (3)
N(1)—C(7)	1.469 (2)		
C(2)—N(1)—C(6)	120.9 (1)	O(2)—C(4)—C(3)	118.0 (2)
C(2)—N(1)—C(7)	121.4 (2)	O(2)—C(4)—C(5)	124.1 (2)
C(6)—N(1)—C(7)	117.6 (2)	C(3)—C(4)—C(5)	117.9 (2)
N(1)—C(2)—C(1)	120.0 (2)	C(4)—C(5)—C(6)	120.4 (2)
N(1)—C(2)—C(3)	118.9 (2)	N(1)—C(6)—C(5)	121.3 (2)
C(1)—C(2)—C(3)	121.1 (2)	N(1)—C(7)—C(8)	111.0 (1)
O(1)—C(3)—C(2)	117.8 (2)	O(3)—C(8)—O(4)	125.3 (2)
O(1)—C(3)—C(4)	121.5 (1)	O(3)—C(8)—C(7)	114.5 (2)
C(2)—C(3)—C(4)	120.6 (2)	O(4)—C(8)—C(7)	120.2 (2)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D	H	*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(1)	H(1)	$O(3^{i})$	0.96 (2)	1.75 (2)	2.677 (2)	160 (2)
O(1)	H(1)	O(2)	0.96 (2)	2.40 (3)	2.732 (2)	100 (2)
O(2)	H(2)	$O(3^{ii})$	1.05 (3)	1.49 (3)	2.545 (2)	176 (3)
C(1)	H(3)	O(1)	0.91 (2)	2.32 (2)	2.786 (3)	112 (2)
C(6)	H(7)	$O(4^{iii})$	1.00 (2)	2.18 (2)	3.155 (3)	165 (2)
C(7)	H(8)	$O(4^{iv})$	0.99 (2)	2.46 (2)	3.387 (3)	156 (1)

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

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985*a*). Data reduction, structure solution, refinement and preparation of material for publication: *TEXSAN* (Molecular Structure Corporation, 1985*b*). Molecular graphics: *ORTEP*II (Johnson, 1976).

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving H atoms, least-squares-planes data and torsion angles, and a stereoview of the molecular packing have been deposited with the IUCr (Reference: CD1062). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of Trimethyloxosulfonium Salts. VIII. New Refinement of the Perchlorate $(CH_3)_3SO^+.ClO_4^-$

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Abstract

The trimethyloxosulfonium cations, $(CH_3)_3SO^+$, have the same geometry as in the other salts reported previously. The ClO_4^- anions occupy two different sites of tetrahedral geometry. The first type is regular [Cl—O bonds 1.402 (2) Å], while the second has an irregular form [Cl—O bonds from 1.379 (5) to 1.417 (3) Å]; two kinds of tetrahedra are located at the site having *m* symmetry with occupation factors of 0.5. The structure of this compound has been solved previously [Coulder, Gantzel & McCullough, (1963). *Acta Cryst.* **16**, 676–681] but the old data required refinement.

Comment

In this series of papers, the iodide, bromide, chloride, nitrate, chromate, chlorocadmate and thiocyanate structures have been reported (Jannin, Puget, de Brauer & Perret, 1991*a*,*b*,*c*; de Brauer, Jannin, Puget

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