Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.300 (5)	O4—C7	1.169 (5)
O1—C4	1.486 (5)	C1—C2	1.532 (5)
O2—C1	1.192 (4)	C2—C3	1.500 (6)
O3—C7	1.355 (5)	C3—C4	1.503 (5)
O3—C2	1.405 (4)	C7—C8	1.485 (6)
C1—O1—C4	109.6 (3)	C3—C2—C1	101.3 (3)
C7—O3—C2	118.8 (3)	C2—C3—C4	100.2 (3)
O2—C1—O1	124.3 (4)	O1—C4—C3	104.0 (3)
O2—C1—C2	126.6 (4)	O4—C7—O3	121.0 (4)
O1—C1—C2	109.1 (3)	O4—C7—C8	124.0 (5)
O3—C2—C3	118.4 (3)	O3—C7—C8	115.0 (4)
O3—C2—C1	109.6 (3)		

The C16 atom is disordered over two positions; the occupancy factor for each position was refined, resulting in a value of 0.83 (6) for C16 and 0.17 (6) for C16′. The positions of all H atoms were computed and refined with an overall isotropic displacement parameter, using a riding model. The enantiomer was defined according to the pharmacological activity of the compound.

Data collection: *CAD-4/PC* (Kretschmar, 1996). Cell refinement: *CAD-4/PC*. Data reduction: *CFEO* (Solans, 1978). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Brueggemann & Schmid, 1990). Software used to prepare material for publication: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1022). Services for accessing these data are described at the back of the journal.

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Three *N*-Aryl-Substituted 3-Hydroxypyridin-4-ones

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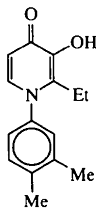
Abstract

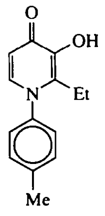
The molecular structures of 1-(3,4-dimethylphenyl)-2-ethyl-3-hydroxypyridin-4-one, $C_{15}H_{17}NO_2$, (1), 2-ethyl-3-hydroxy-1-(4-methylphenyl)pyridin-4-one, $C_{14}H_{15}NO_2$, (2), and 2-ethyl-3-hydroxy-1-(4-methoxyphenyl)pyridin-4-one, $C_{14}H_{15}NO_3$, (3), have been determined. The compounds all exhibit mutually hydrogen-bonded dimeric pairs. In the case of (1), the molecules of the dimer are symmetry related, while in (2) and (3) two independent molecules of the asymmetric unit are linked.

Comment

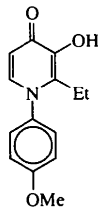
The structures form dimeric units through mutual O1—H1···O2 hydrogen bonds (Fig. 1). This type of dimeric structure is commonly found for the anhydrous 3-hydroxypyridin-4-ones (Hider *et al.*, 1990; Chan *et al.*, 1992; Xiao *et al.*, 1992; Burgess *et al.*, 1993) and 3-hydroxypyran-4-ones, which are also reported as hydrogen-bonded chains (Burgess *et al.*, 1996; Brown *et al.*, 1995).



(1)



(2)



(3)

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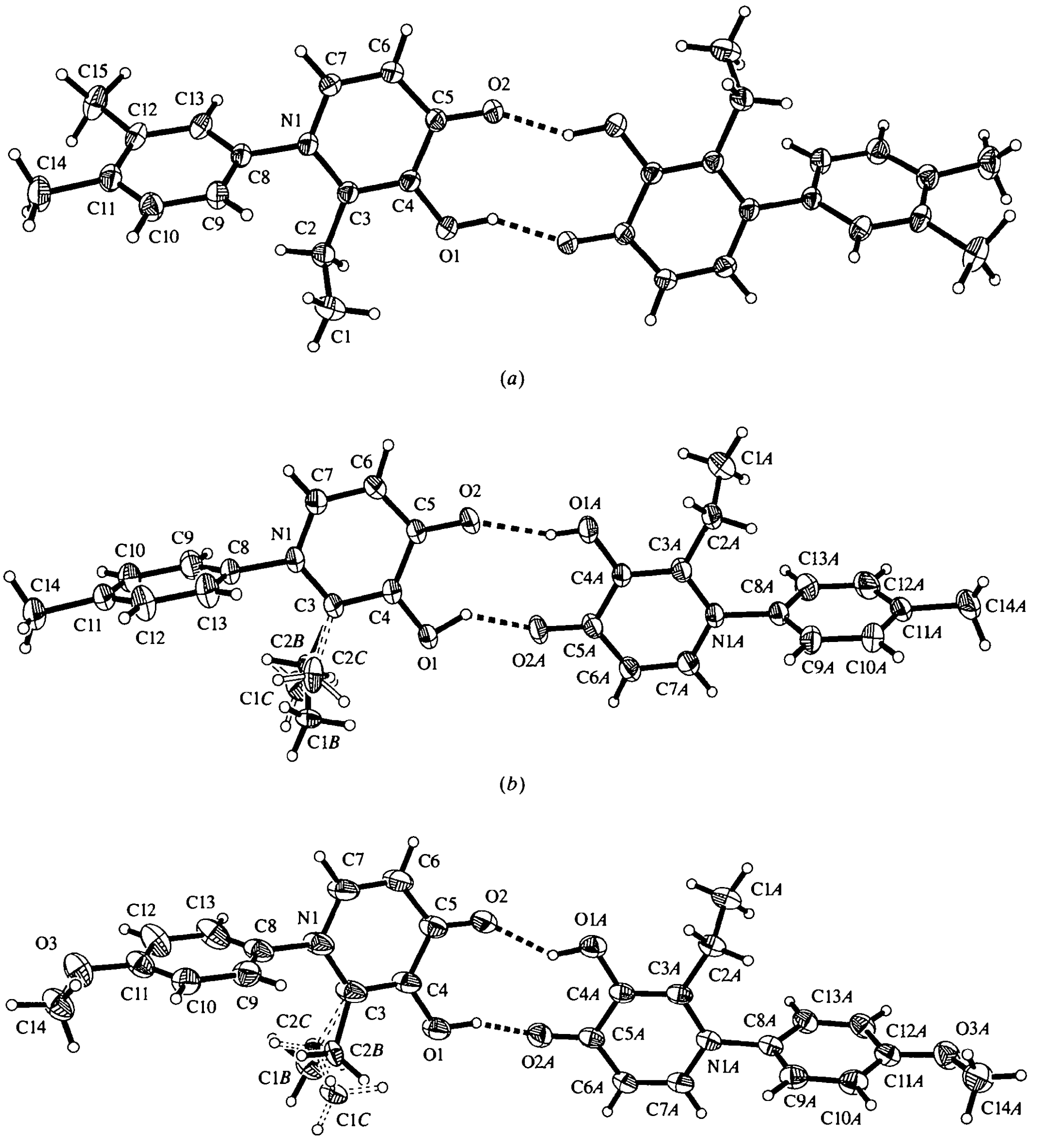
Important bond distances in compounds (1), (2) and (3) are essentially the same within experimental error, but show small yet significant differences compared with the *N*-methyl analogue (4) (Table 1). In the potentially coordinating OCCO fragment, the difference between the two C—O bond distances is greater for the *N*-phenyl (0.093–0.104 Å) derivatives than for the *N*-methyl compound (0.075 Å), and the C—C bond distances are longer for the *N*-phenyl derivatives than for the *N*-methyl. These small differences are consistent with slightly more delocalization in the *N*-phenyl compounds than in the *N*-methyl compound.

In the case of (1), the halves of the dimeric pair are related by a centre of symmetry at $0,\frac{1}{2},0$ and therefore (1) has two equivalent O1—H1···O2 hydrogen bonds where the O···O distances are 2.692 (2) Å. For both (2) and (3), the two independent molecules of the asymmetric unit are linked, with O···O distances of 2.686 (3), 2.688 (3) and 2.635 (3), 2.654 (3) Å, respectively. For all structures, the bridging H atoms were located as the highest residual electron density when all other atoms were included in the refinement. For all three structures, the dimers are further linked by weak C—H···O contacts of *ca* C···O 3.3 Å, as previously observed for this



(*a*)

(*b*)

(*c*)

Fig. 1. The molecular structures of (*a*) dimer (1), (*b*) compound (2) and (*c*) compound (3) showing the atom-numbering schemes and 30% displacement ellipsoids. Intermolecular O—H···O bonds are shown as dashed lines. H atoms are drawn as spheres of arbitrary radii. For (2) and (3), the disorder of the ethyl group is shown with open dashed lines.

type of compound (Burgess *et al.*, 1996). One of the molecules of both (2) and (3) exhibit disorder of the ethyl groups: C2*B* and C1*C* lie above and C1*B* and C2*C* below the ring plane, each with 50% occupancy of its site. For these structures, steric hindrance dictates that the rings must be rotated from coplanarity about the N1—C8 bond. For (1), the interplanar angle between the phenyl and pyridinone rings is 65.7 (1)°. In (2) and (3), the corresponding interplanar angles are 88.9 (1) and 89.5 (1), and 75.7 (1) and 86.1 (1)°, respectively.

Experimental

Compounds (1), (2) and (3) were prepared by the reaction of ethyl maltol (4.2 g, 30 mmol) with the appropriate amine (60 mmol) in dilute HCl (50 ml) under reflux for 72 h followed by hot filtration. Crystals suitable for X-ray analysis were obtained from hot methanol.

Compound (1)

Crystal data

$C_{15}H_{17}NO_2$
$M_r = 243.30$
Monoclinic
$P2_1/c$
$a = 9.197$ (1) Å
$b = 10.606$ (1) Å
$c = 13.259$ (1) Å
$\beta = 90.94$ (1)°
$V = 1293.2$ (2) Å^3
$Z = 4$
$D_x = 1.250$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 27 reflections
$\theta = 4.6$–$12.4°$
$\mu = 0.083$ mm^{-1}
$T = 293$ (2) K
Block
0.69 × 0.42 × 0.38 mm
Colourless

Data collection

Siemens *P*4 four-circle diffractometer
ω scans
Absorption correction: none
2466 measured reflections
1803 independent reflections
1515 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.014$
$\theta_{\rm max} = 23°$
$h = -1 \rightarrow 10$
$k = -1 \rightarrow 11$
$l = -14 \rightarrow 14$
3 standard reflections every 100 reflections intensity variation: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.121$
$S = 1.056$
1803 reflections
163 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.4658P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.007$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (2)

Crystal data

$C_{14}H_{15}NO_2$
$M_r = 229.27$
Monoclinic
$C2/c$
$a = 7.305$ (1) Å
$b = 18.615$ (7) Å
$c = 18.296$ (2) Å
$\beta = 99.81$ (2)°
$V = 2451.6$ (10) Å^3
$Z = 8$
$D_x = 1.242$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 5.0$–$12.3°$
$\mu = 0.083$ mm^{-1}
$T = 293$ (2) K
Block
0.49 × 0.38 × 0.33 mm
Colourless

Data collection

Siemens *P*4 four-circle diffractometer
ω scans
Absorption correction: none
4303 measured reflections
3118 independent reflections
1885 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.025$
$\theta_{\rm max} = 23.5°$
$h = -1 \rightarrow 7$
$k = -1 \rightarrow 20$
$l = -20 \rightarrow 20$
3 standard reflections every 100 reflections intensity variation: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.148$
$S = 1.017$
3117 reflections
326 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2 + 1.4167P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = -0.055$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0037 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (3)

Crystal data

$C_{14}H_{15}NO_3$
$M_r = 245.27$
Triclinic
$P\bar{1}$
$a = 7.306$ (1) Å
$b = 10.351$ (1) Å
$c = 17.321$ (2) Å
$\alpha = 86.25$ (1)°
$\beta = 78.44$ (1)°
$\gamma = 71.92$ (1)°
$V = 1219.9$ (2) Å^3
$Z = 4$
$D_x = 1.335$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 38 reflections
$\theta = 2.7$–$12.5°$
$\mu = 0.094$ mm^{-1}
$T = 293$ (2) K
Block
0.68 × 0.47 × 0.32 mm
Colourless

Data collection

Siemens *P*4 four-circle diffractometer
ω scans
Absorption correction: none
4353 measured reflections
3413 independent reflections
2584 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.016$
$\theta_{\rm max} = 24.93°$
$h = -1 \rightarrow 8$
$k = -12 \rightarrow 11$
$l = -18 \rightarrow 19$
3 standard reflections every 100 reflections intensity variation: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.143$
$S = 1.071$
3400 reflections
343 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.5731P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.014$
$\Delta\rho_{\max} = 0.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond distances (Å) for compounds (1), (2), (3) and (4)*

		(1)	(2)[a]	(3)[a]	(4)
O1	C4	1.357 (2)	1.36 (5)	1.357 (3)	1.350 (4)
O1*A*	C4*A*		1.358 (5)	1.359 (3)	
O2	C5	1.260 (2)	1.259 (4)	1.264 (3)	1.275 (4)
O2*A*	C5*A*		1.254 (4)	1.260 (3)	
N1	C8	1.451 (2)	1.457 (4)	1.446 (4)	1.480 (5)
N1*A*	C8*A*		1.457 (4)	1.451 (3)	
C3	C4	1.365 (3)	1.359 (4)	1.366 (4)	1.375 (5)
C3*A*	C4*A*		1.360 (4)	1.365 (4)	
C4	C5	1.435 (3)	1.428 (5)	1.432 (4)	1.410 (5)
C4*A*	C5*A*		1.437 (5)	1.431 (4)	

Note: (*a*) two independent molecules.

Table 2. *Hydrogen-bonding geometry (Å, °) for (1), (2) and (3)*

Compound	D—H···A	H···A	D···A	D—H···A
(1)	O1—H1···O2^{i}	1.72	2.692 (2)	151
(2)	O1—H1···O2*A*	1.84	2.686 (3)	140
	O1*A*—H1*A*···O2	1.88	2.688 (3)	156
(3)	O1—H1*A*···O2*A*	1.64	2.635 (3)	162
	O1*A*—H1*AA*···O2	1.82	2.654 (3)	142

Symmetry code: (i) $1 - x, -y, 1 - z$

For compound (3), the data collection initially had $\theta_{\max} = 25°$, but it became obvious that no useful diffraction was occurring above $\theta = 22.5°$, so this limit was adopted thereafter. For all three structures, the bridging hydroxyl H atoms were located from difference Fourier syntheses. The positions of the disordered H atoms on C15 for (1) and the H atoms on the disordered methyl C atoms C1*B* and C1*C* for (3) were also located from difference Fourier maps. The remaining H atoms were introduced at geometrically calculated positions (C—H = 0.96 Å). All H atoms were then refined using riding models with a single fixed value for $U_{\rm iso} = 0.08$ Å^2.

For all compounds, data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990*a*); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXTL/PC*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1164). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 433–436

Inclusion Complex of *rac*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane with Hydrochloride and Water

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Abstract

In the crystal structure of the title compound, $C_{16}H_{38}N_4^{2+}.2Cl^-.3H_2O$, a rather complex hydrogen-bonding network is observed. The macrocycle is stabilized as a dication, 5,5,7,12,12,14-hexamethyl-1,8-diaza-4,11-diazoniacyclotetradecane, forming N—H···Cl and N—H···O hydrogen bonds. The water molecules are distinguished by their inequality in structure formation. They are involved in different types of intermolecular hydrogen bonding in the crystal lattice.

Comment

The field of coordination chemistry of polyazamacrocycles has undergone spectacular growth since the early 1960s, following the pioneering contribution of Curtis (1964). The macrocyclic ligand 5,5,7,12,12,14-