organic compounds

N-(2-Methoxy-6-oxo-1,6-dihydro-pyrimidin-4-yl)formamide: hydrogen-bonded sheets of centrosymmetric $R_2^2(8)$ and $R_6^4(28)$ rings

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Molecules of the title compound, $C_6H_7N_3O_3$, are linked into sheets of centrosymmetric $R_2^2(8)$ and $R_6^4(28)$ rings by two nearly linear N—H···O hydrogen bonds [H···O = 1.91 and 1.98 Å, N···O = 2.786 (3) and 2.862 (3) Å, and N—H···O = 175 and 177°].

Comment

With the aim of preparing intermediates for the synthesis of new fused pyrimidines, we have applied the formylation procedure using formic acetic anhydride to the preparation of 5-formylpyrimidine derivatives (Negrillo *et al.*, 1988), but when 6-amino-2-methoxypyrimidin-4(3H)-one was used as starting material, the title compound, (I) (Fig. 1), was obtained selectively in 73% yield. We report here the molecular and supramolecular structure of (I).

(I)
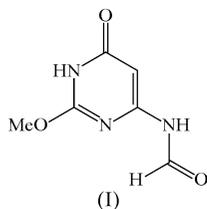
The bond distances within the pyrimidinone ring of (I) (Table 1) provide clear evidence of strong bond fixation. Thus, the N1—C2 bond is very much shorter than any of the C2—N3, N3—C4, N1—C6 or C6—N6 bonds, and the C5—C6 bond is very much shorter than the C4—C5 bond. However, the exocyclic C4—O4 bond is significantly longer than the formyl C61—O6 bond, even though N3—C4 is somewhat longer than N6—C61. This may be connected with the disorder of the H atom bonded to N6, which appears to be spread over a range of N—H distances. The disorder was modelled using two sites

for this H atom, one adjacent to N6 with occupancy 0.73 (5) and the other almost midway along an intermolecular N···H···O contact with occupancy 0.27 (5). At each of C2, C4 and C6, the two exocyclic bond angles are markedly different, with the maximum difference of nearly 10° at C2. With the exception of the methyl H atoms, the entire molecule is effectively planar.

The supramolecular aggregation is very simple, depending upon just two N—H···O hydrogen bonds, both involving the same amidic atom O4 as the acceptor, and both of them almost linear (Table 2). It is striking that atom O4 forms the longer of the two amidic C—O bonds and that neither formyl atom O6 nor methoxy atom O2 acts as an acceptor of hydrogen bonds. The overall supramolecular aggregation is not affected by the partial disorder of H6.
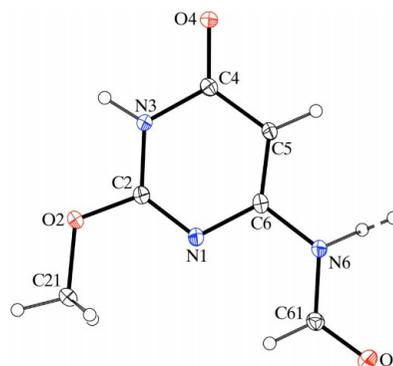
Figure 1
A molecule of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The two sites shown for the H atom bonded to N6 have occupancies of 0.73 (5) and 0.27 (5), respectively (see *Comment*).
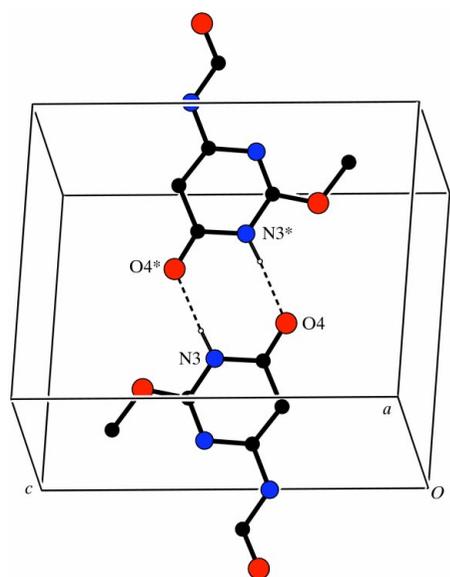
Figure 2
Part of the crystal structure of compound (I), showing the formation of an $R_2^2(8)$ dimer centred at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position (1 − x, 1 − y, 1 − z).

The formation of the two-dimensional supramolecular structure is readily analysed in terms of a centrosymmetric dimer unit as the basic building block. Ring atom N3 in the molecule at (x, y, z) acts as hydrogen-bond donor to amidic atom O4 in the molecule at $(1 - x, 1 - y, 1 - z)$, so forming a centrosymmetric $R_2^2(8)$ (Bernstein *et al.*, 1995) dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 2). Exocyclic atoms N6 in the molecules at (x, y, z) and $(1 - x, 1 - y, 1 - z)$, which form the dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, act as donors to atoms O4 in the molecules at $(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ and $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$, respectively, which themselves form parts of the $R_2^2(8)$ dimers centred at $(0, 0, 0)$ and $(1, 1, 1)$, respectively. Similarly, atoms O4 in the molecules at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ accept hydrogen bonds from atoms N6 in the molecules at $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$ and $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, which themselves form parts of the dimers centred at $(0, 1, 0)$ and $(1, 0, 1)$, respectively. Propagation of these two hydrogen bonds then generates a $(10\bar{1})$ sheet built of centrosymmetric $R_2^2(8)$ and $R_6^4(28)$ rings (Fig. 3). There are no direction-specific interactions between adjacent sheets.
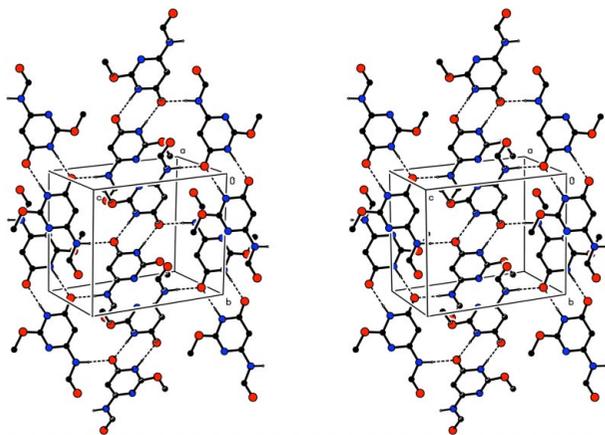
Figure 3
A stereoview of part of the crystal structure of compound (I), showing the formation of a $(10\bar{1})$ sheet of $R_2^2(8)$ and $R_6^4(28)$ rings. For the sake of clarity, atom H6*A* and H atoms bonded to C atoms have all been omitted.

Experimental

6-Amino-2-methoxypyrimidin-4(3*H*)-one (1.41 g, 10 mmol) was added to a mixture of formic acid (1.33 ml, 40 mmol) and acetic anhydride (4 ml, 40 mmol) and the mixture was heated under reflux for 90 min. The mixed solvents were removed under reduced pressure to give an orange solid, which was recrystallized from ethanol (400 ml) to give a microcrystalline yellow solid. Yellow needles of (I) suitable for single-crystal X-ray diffraction were grown from a solution in dimethyl sulfoxide (yield 73%). Accurate mass by MS (IE 70 eV): *m*/*z* found 169.0482, $C_6H_7N_3O_3$ requires 169.0487.

Crystal data

$C_6H_7N_3O_3$	$D_x = 1.578$ Mg m^{-3}
$M_r = 169.15$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 1627
$a = 7.0515\,(7)$ Å	reflections
$b = 9.0031\,(12)$ Å	$\theta = 5.0$–$27.5°$
$c = 11.237\,(2)$ Å	$\mu = 0.13$ mm^{-1}
$\beta = 93.690\,(11)°$	$T = 120\,(2)$ K
$V = 711.91\,(17)$ Å^3	Block, colourless
$Z = 4$	$0.33 \times 0.14 \times 0.11$ mm

Data collection

Nonius KappaCCD area-detector diffractometer	1627 independent reflections
	905 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.067$
Absorption correction: multi-scan (*EVALCCD*; Duisenberg *et al.*, 2003)	$\theta_{max} = 27.5°$
	$h = -8 \rightarrow 9$
	$k = -11 \rightarrow 11$
$T_{min} = 0.962$, $T_{max} = 0.986$	$l = -14 \rightarrow 14$
9104 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2 + 0.3784P]$
$R[F^2 > 2\sigma(F^2)] = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.147$	
$S = 1.11$	$(\Delta/\sigma)_{max} < 0.001$
1627 reflections	$\Delta\rho_{max} = 0.41$ e Å^{-3}
110 parameters	$\Delta\rho_{min} = -0.39$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.289 (3)	C2—O2	1.324 (3)
C2—N3	1.353 (3)	O2—C21	1.452 (3)
N3—C4	1.379 (3)	C4—O4	1.257 (3)
C4—C5	1.406 (3)	C6—N6	1.389 (3)
C5—C6	1.357 (3)	N6—C61	1.361 (3)
C6—N1	1.365 (3)	C61—O6	1.213 (3)
N1—C6—N6—C61	1.5 (3)	C6—N6—C61—O6	178.4 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3$\cdots$O4^i	0.88	1.91	2.786 (3)	175
N6—H6$\cdots$O4^{ii}	0.88	1.98	2.862 (3)	177

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

The space group $P2_1/n$ was uniquely assigned from the systematic absences. All H atoms were located in difference maps. H atoms bonded to C atoms were treated as riding atoms, with C—H distances of 0.95 (aromatic and formyl) or 0.98 Å (methyl) and with $U_{iso}(H) = 1.2$ or $1.5U_{eq}(C)$. The H atom bonded to N3 was permitted to ride at the distance deduced from difference maps (0.88 Å), with $U_{iso}(H) = 1.2U_{eq}(N)$. The H atom formally bonded to N6 was found to be disordered over two sites, one adjacent to N6 and denoted H6 and the other, denoted H6*A*, approximately midway between N6 and atom O4 of a neighbouring molecule at $(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$. The coordinates of these two sites were initially refined with the occupancies tied to sum to unity; in the final cycles of refinement, their positions were fixed, with $U_{iso}(H) = 1.2U_{eq}(N6)$. The site occupancies for H6 and H6*A* refined to 0.73 (5) and 0.27 (5), respectively. A difference map calculated with these two sites, H6 and H6*A*, omitted shows an extended ridge of electron density between these two sites, possibly suggesting a very large amplitude motion of this H atom.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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