

Methyl 4-amino-2,3-dihydro-6-methoxy-1,3-dioxo-1*H*-pyrrolo[3,4-*c*]-pyridine-7-carboxylate forms hydrogen-bonded sheets built from $R_2^2(8)$ and $R_6^6(42)$ rings

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In the title compound, $C_{10}H_9N_3O_5$, which was formed by the reaction of 6-amino-2-methoxy-4(3*H*)-pyrimidinone with dimethyl acetylenedicarboxylate, the molecules are linked by $N-H\cdots O$ hydrogen bonds [$N\cdots O$ 2.8974 (15) and 3.0300 (15) Å, and $N-H\cdots O$ 165 and 174°] into planar sheets built from alternating $R_2^2(8)$ and $R_6^6(42)$ rings.

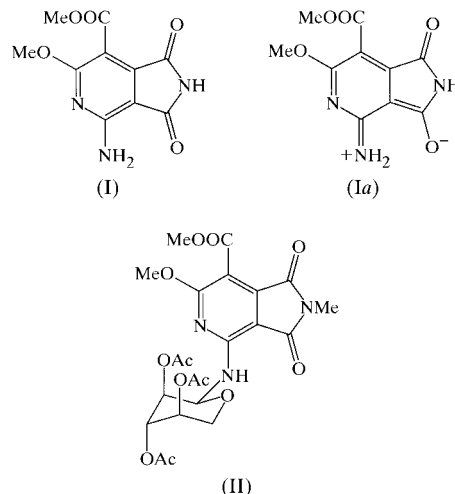
Comment

The title compound, (I), was obtained from the reaction between 6-amino-2-methoxy-4(3*H*)-pyrimidinone and dimethyl acetylenedicarboxylate (see reaction scheme), and the structure determination reported here provides definitive proof of the constitution of (I) not readily obtained from spectroscopic data alone. It also allows comparison between (I) and the substituted analogue (II) (Low *et al.*, 2001). Thirdly, it reveals an almost planar hydrogen-bonded network made up of alternating large and small rings.

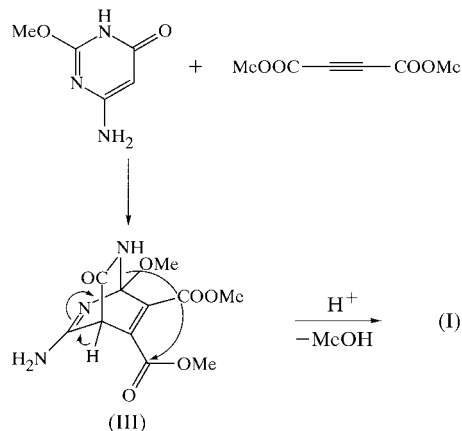
The bicyclic molecules of (I) (Fig. 1) are essentially planar, except for the methyl carboxylate group, which is significantly twisted out of the ring plane (Table 1). A similar twist of this substituent was observed in compound (II), where the C—C—C—O torsion angles involving the carbonyl O atom are $-58.1(7)$ and $120.0(7)^\circ$. The formation of (I) is most simply rationalized (see reaction scheme) in terms of a hetero Diels–Alder reaction to give the bicyclic intermediate, (III), followed by acid-catalysed rearrangement with loss of methanol to give (I).

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The bond lengths in (I) (Table 1) provide clear evidence of electron delocalization between certain of the substituents: C3—O3 is significantly longer than C1—O1, C3—C3a is significantly shorter than C1—C7a, and C4—N4 is not only significantly shorter than C4—N5, but its distance is less than



the lower quartile value of 1.340 Å (Allen *et al.*, 1987) for aryl— NH_2 bonds. In addition, C3a—C4 is significantly longer than C7—C7a. These features taken together, all of which are closely reproduced in (II), point to the important contribution of the canonical form (Ia) to the overall electronic structure of this bicyclic system. The development of form (Ia) is accompanied by the formation of a weak intramolecular hydrogen bond (Table 2); although the $N\cdots O$ distance is necessarily rather long, as it is constrained by the geometry of the covalently bonded molecular framework, this hydrogen bond is charge-enhanced, since both the donor and the acceptor are charged in form (Ia). The metrical similarities between (I) and (II), despite their different N-substituents, suggest that delocalization of this kind may be typical for compounds of this type.



The molecules of (I) are linked by two $N-H\cdots O$ hydrogen bonds (Table 2) into two-dimensional sheets. The amino N4 atom acts as donor, *via* H4A, to carboxyl O71ⁱⁱ [symmetry code: (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$], while N4ⁱⁱⁱ in turn acts as donor to O71ⁱⁱⁱ [symmetry code: (iii) $x, 1 + y, z$]. In this manner, a

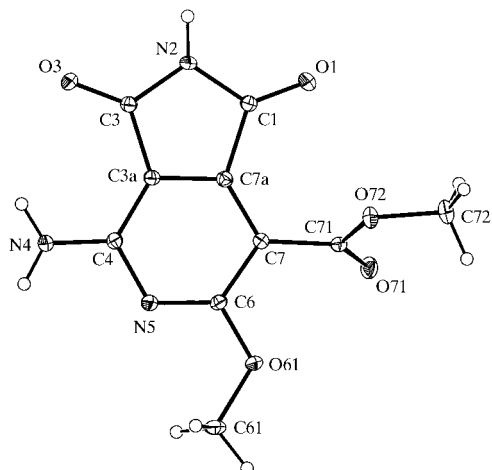


Figure 1

The molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

$C(8)$ spiral chain is produced, running parallel to the $[010]$ direction and generated by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{3}{2})$ (Fig. 2). The other $N-H \cdots O$ hydrogen bond generates centrosymmetric $R_2^2(8)$ rings: imino N2 acts as donor to carbonyl O3ⁱ [symmetry code: (i) $2 - x, -y, 1 - z$], while N2ⁱ is donor to O3, so generating a ring centred at $(1, 0, \frac{1}{2})$ (Fig. 2). The combination of these two motifs, each built from a single hydrogen bond, generates a continuous sheet (Fig. 2) in which the $R_2^2(8)$ rings alternate with centrosymmetric $R_6^6(42)$ rings.

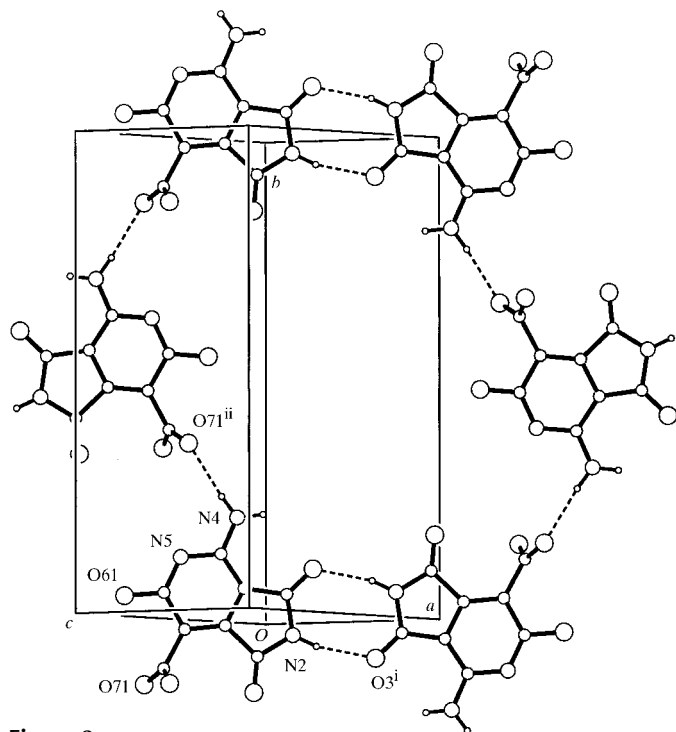


Figure 2

Part of the crystal structure of (I), showing the $R_2^2(8)$ and $R_6^6(42)$ rings which form the (103) sheets. For the sake of clarity, the methyl C atoms and H atoms bonded to C atoms have been omitted [symmetry codes: (i) $2 - x, -y, 1 - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$].

Each molecule is hydrogen bonded to three others. If single molecules are regarded as the nodes of the resulting net, then this is of the $(6,3)$ type (Batten & Robson, 1998), while if the centrosymmetric $R_2^2(8)$ dimers are regarded as the nodes, then the net is of the $(4,4)$ type. Although each molecule contains three $N-H$ bonds and three carbonyl groups, carbonyl O1 does not participate in hydrogen bonds. In terms of the canonical forms (I) and (Ia), it is notable that of the chemically similar atoms O1 and O3, only the charged atom O3 acts as a hydrogen-bond acceptor.

The sheets are nearly planar and lie parallel to (103) . The formation of each sheet utilizes $\frac{4}{3}$ molecules per unit cell, so that with $Z = 4$, three such sheets are required to define the structure fully. Adjacent sheets are not interwoven, despite the presence of the $R_6^6(42)$ rings, but there are aromatic $\pi-\pi$ -stacking interactions between molecules in adjacent sheets. The molecule at (x, y, z) forms a $\pi-\pi$ -stacking interaction with the molecule at $(1 - x, -y, 1 - z)$, which forms part of an adjacent sheet. The perpendicular distance between these molecular planes is $3.335(3)$ Å, and the centroid offset between the five-membered rings in the two molecules is *ca* 0.84 Å, while the centroid offset between the five-membered ring in one molecule and the six-membered ring in the other, which carry opposite net charges [see (Ia) in scheme above], is *ca* 1.60 Å (Fig. 3). Propagation of this $\pi-\pi$ interaction by the space group serves to link all the sheets into a single three-dimensional framework.

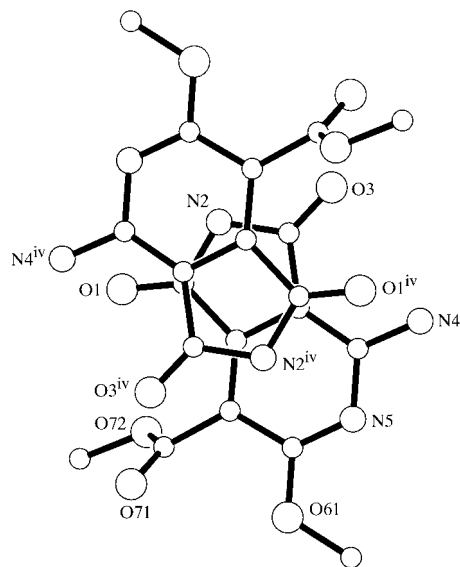


Figure 3

Part of the crystal structure of (I) showing the $\pi-\pi$ -stacking interaction. For the sake of clarity, H atoms bonded to C atoms have been omitted [symmetry code: (iv) $1 - x, -y, 1 - z$].

Experimental

Dimethyl acetylenedicarboxylate (2.84 g, 20 mmol) was added to a suspension of 6-amino-2-methoxy-4(3*H*)-pyrimidinone (1.41 g, 10 mmol) in dioxane (40 ml) containing a catalytic amount of trifluoroacetic acid (0.29 g, 2.5 mmol). The mixture was stirred at 358 K for 12 h. The solvent was evaporated under reduced pressure and

compound (I) was isolated and purified by flash column chromatography on silica gel using methylene chloride/ethyl ether (7:3 v/v) as eluent (yield: 0.58 g, 23%). Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution in methanol [m.p. 529 K (decomposition)]. Analysis, found: C 47.9, H 3.6, N 16.7%; C₁₀H₉N₃O₅ requires: C 47.8, H 3.6, N 16.7%.

Crystal data

C₁₀H₉N₃O₅ $D_x = 1.602 \text{ Mg m}^{-3}$
 $M_r = 251.20$ Mo $K\alpha$ radiation
 Monoclinic, $P2_1/n$ Cell parameters from 2309 reflections
 $a = 6.8189 (2) \text{ \AA}$ $\theta = 3.29\text{--}27.45^\circ$
 $b = 16.1505 (4) \text{ \AA}$ $\mu = 0.131 \text{ mm}^{-1}$
 $c = 9.6257 (3) \text{ \AA}$ $T = 150 (2) \text{ K}$
 $\beta = 100.7612 (13)^\circ$ Block, colourless
 $V = 1041.42 (5) \text{ \AA}^3$ $0.2 \times 0.2 \times 0.2 \text{ mm}$
 $Z = 4$

Data collection

KappaCCD area-detector diffractometer 2309 independent reflections
 1913 reflections with $I > 2\sigma(I)$
 φ and ω scans with κ offsets $R_{\text{int}} = 0.030$
 Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997) $\theta_{\text{max}} = 27.45^\circ$
 $T_{\text{min}} = 0.974$, $T_{\text{max}} = 0.974$ $h = -8 \rightarrow 8$
 8132 measured reflections $k = -20 \rightarrow 20$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.2574P]$
 $R[F^2 > 2\sigma(F^2)] = 0.041$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.113$ $(\Delta/\sigma)_{\text{max}} = 0.001$
 $S = 1.05$ $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
 2309 reflections $\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
 165 parameters
 H-atom parameters constrained

Table 1

Selected geometric parameters (\AA , $^\circ$).

C1—N2	1.3844 (17)	C3a—C4	1.4009 (18)
N2—C3	1.3847 (17)	C4—N5	1.3607 (18)
C1—C7a	1.5068 (18)	N5—C6	1.3181 (17)
C3—C3a	1.4569 (18)	C6—C7	1.4247 (18)
C3a—C7a	1.3901 (18)	C7—C7a	1.3684 (19)
C1—O1	1.2082 (17)	C4—N4	1.3334 (17)
C3—O3	1.2266 (16)		
C6—C7—C71—O71	65.65 (19)	C7—C71—O72—C72	-174.85 (11)
C6—C7—C71—O72	-114.48 (14)	C7—C6—O61—C61	172.57 (11)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N2—H2 \cdots O3 ⁱ	0.88	2.04	2.8974 (15)	165
N4—H4A \cdots O71 ⁱⁱ	0.88	2.15	3.0300 (15)	174
N4—H4B \cdots O3	0.88	2.49	3.0973 (15)	126

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

H atoms were treated as riding, with C—H = 0.98 and N—H = 0.88 \AA .

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton. The authors thank the staff for all their help and advice.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1042). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
 Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed. Engl.* **37**, 1460–1494.
 Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
 Low, J. N., Garcia, C., Melguizo, M., Cobo, J., Noguera, M., Sanchez, A., López, M. D. & Light, M. E. (2001). *Acta Cryst.* **C57**, 222–224.
 Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
 Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
 Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
 Spek, A. L. (2000). *PLATON*. University of Utrecht, The Netherlands.