Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

4-Amino-5-(2-hydroxy-4,4-dimethyl-6-oxocyclohexenylmethyl)-1-methyl-2-(methylsulfanyl)pyrimidin-6(1*H*)-one: hydrogen-bonded chains are π-stacked in pairs

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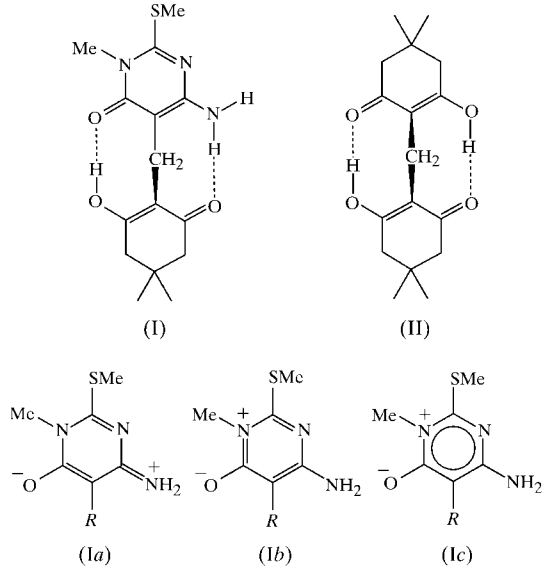
Received 13 January 2004
Accepted 15 January 2004
Online 10 February 2004

Molecules of the title compound, $C_{15}H_{21}N_3O_3S$, have a markedly polarized electronic structure; the carbocyclic ring adopts an envelope conformation and the overall molecular conformation appears to be controlled by two intramolecular hydrogen bonds, one each of the O—H···O and N—H···O types. The molecules are linked into *C*(6) chains by an intermolecular N—H···O hydrogen bond, and pairs of these hydrogen-bonded chains are linked by a π–π stacking interaction.

Comment

As part of a program for the synthesis of fused pyrimido derivatives, we have investigated the three-component cyclocondensation between 4-amino-1-methyl-2-(methylsulfanyl)-pyrimidin-6(1*H*)-one, formaldehyde and 5,5-dimethylcyclohexane-1,3-dione (dimedone), but instead of the desired pyrimido[3,4-*b*]quinoline, the intermediate title compound, (I), was obtained. We report here its molecular and supramolecular structure. Three-component reactions of this general type can also provide, as a by-product, the twofold symmetrical compound 2,2′-methylenebis(5,5-dimethyl-3-hydroxy-2-cyclohexen-1-one), (II), whose structure we have reported recently (Low *et al.*, 2003).

Within the heterocyclic ring of (I), the C4—C5 and C5—C6 distances (Table 1) are similar, and they cannot be associated readily with double and single bonds, respectively. In addition, the C4—N4 distance is very much shorter than the mean value (1.355 Å; Allen *et al.*, 1987) for bonds of type C(aryl)—NH_2, where N is planar. In contrast to the C—C bonds, the C2—N3 and N3—C4 bonds have distances typical of those for localized double and single bonds of these types. While the C6—O6 distance is typical of those in unstrained amides, the C6—N1 distance is very long for its type (mean value 1.346 Å; Allen *et al.*, 1987). These values, taken together, point to the significance of the polar form (I*a*) as an important contributor to the overall molecular–electronic structure but effectively eliminate as contributors other forms, such as (I*b*) and (I*c*).



There is clear evidence for bond fixation in the atom sequence between O52 and O56. Within the carbocyclic ring, the total puckering amplitude, *Q*, is 0.455 (2) Å, markedly less than the value (0.63 Å) for an ideal cyclohexane chair of $\overline{3}m$ (D_{3d}) molecular symmetry, with C—C distances of 1.54 Å (Cremer & Pople, 1975). For the atom sequence C51 to C56, the angular parameters [θ = 53.9 (3)° and φ = 195.8 (4)°] are clearly indicative of the sofa or envelope conformation being the best single qualitative descriptor, with a local pseudo-mirror plane passing through atoms C5, C54, C541 and C542 (Fig. 1); this conformation is confirmed by the leading torsion angles involving this ring (Table 1). However, the envelope conformation can itself be represented as a linear combination of the three primitive forms chair, boat and twist-boat (Evans & Boeyens, 1989), with the chair form dominant here.

There are three hydrogen bonds (Table 2), two of which are intramolecular, and these doubtless control the overall molecular conformation, in particular, the twist angles about the C5—C57 and C51—C57 bonds (Table 1). The short O···O distance in the intramolecular O—H···O hydrogen bond is consistent with the development of a significant negative charge on atom O6 [*cf.* form (I*a*)]. Each of the intramolecular hydrogen bonds gives rise to an independent *S*(8) motif (Bernstein *et al.*, 1995). The molecules are linked into chains by a single intermolecular N—H···O hydrogen bond; amine atom N4 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor, *via* atom H4*B*, to amide atom O6 in the molecule at

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 DOI: 10.1107/S0108270104001118

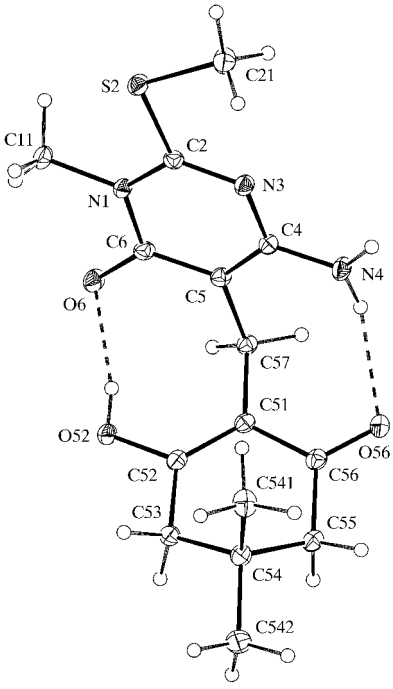

Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

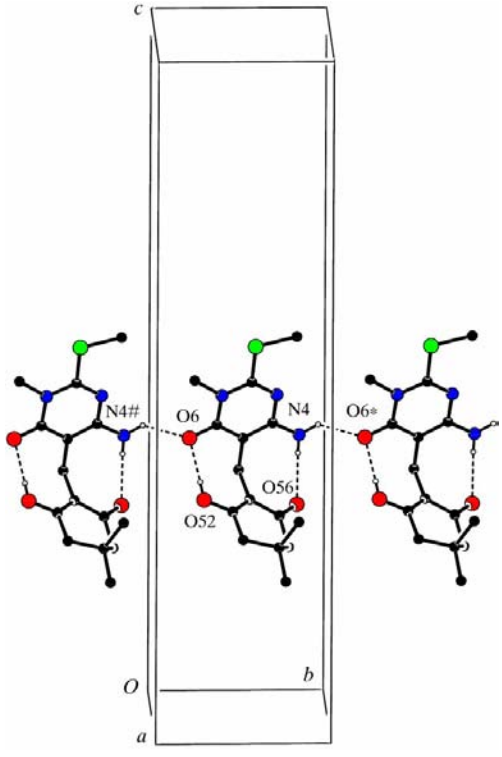

Figure 2
Part of the crystal structure of (I), showing the formation of a $C(6)$ chain along [010]. For clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, 1 + y, z)$ and $(x, -1 + y, z)$, respectively.

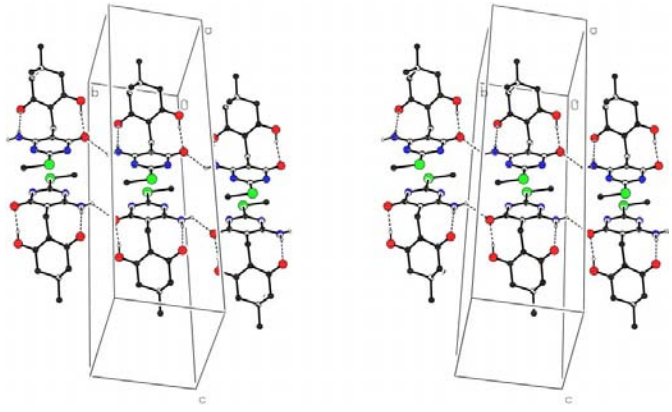

Figure 3
A stereoview of part of the crystal structure of (I), showing the π-stacked double chain in the domain $0.24 < z < 0.76$. For clarity, H atoms bonded to C atoms have been omitted.

$(x, 1 + y, z)$, so generating by translation a $C(6)$ chain running parallel to the [010] direction (Fig. 2).

Four of these chains pass through each unit cell, and they are linked into pairs by a single π–π stacking interaction. The pyrimidine rings of the molecules at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ are parallel, with an interplanar spacing of 3.498 (2) Å. The centroid separation is 3.646 (2) Å, corresponding to a centroid offset of 1.028 (2) Å. The resulting pair of π-stacked chains (Fig. 3) lies in the domain $0.24 < z < 0.76$, and a second double chain, related to the first by the translational symmetry operators, lies in the domain $0.74 < z < 1.26$. There are no direction-specific interactions between the double chains.

Experimental

To a hot solution of 4-amino-1-methyl-2-(methylsulfanyl)pyrimidin-6(1*H*)-one (2 mmol) in ethanol (20 ml, 96%) were added formaldehyde (2 mmol) and dimedone (2 mmol); the reaction mixture was heated under reflux for 4 h. The white powder that formed during the reaction was filtered off and the remaining solution was cooled to 270 K. After 2 d, a white solid was filtered off and recrystallized from ethanol, affording crystalline needles suitable for single-crystal X-ray diffraction (yield 30%; m.p. 426–428 K). Analysis found: C 55.7, H 6.7, N 12.8, S 9.9%; $C_{15}H_{21}N_3O_3S$ requires: C 55.7, H 6.6, N 13.0, S 9.9%.

Crystal data

$C_{15}H_{21}N_3O_3S$
$M_r = 323.41$
Monoclinic, $P2_1/n$
$a = 7.5524$ (2) Å
$b = 7.1370$ (3) Å
$c = 28.6208$ (11) Å
$\beta = 93.128$ (2)°
$V = 1540.4$ (1) Å^3
$Z = 4$
$D_x = 1.394$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3586 reflections
$\theta = 3.4$–28.2°
$\mu = 0.23$ mm^{-1}
$T = 120$ (2) K
Needle, colourless
0.50 × 0.30 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{min} = 0.868$, $T_{max} = 0.956$
18 675 measured reflections
3586 independent reflections
2600 reflections with $I > 2\sigma(I)$
$R_{int} = 0.071$
$\theta_{max} = 28.2°$
$h = -9 \rightarrow 9$
$k = -8 \rightarrow 9$
$l = -37 \rightarrow 37$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.5167P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.110$	$\Delta\rho_{max} = 0.28$ e Å^{-3}
$S = 1.01$	$\Delta\rho_{min} = -0.29$ e Å^{-3}
3586 reflections	
204 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.334 (2)	N1—C11	1.447 (2)
C2—N3	1.282 (2)	C4—N4	1.319 (2)
N3—C4	1.375 (2)	C6—O6	1.234 (2)
C4—C5	1.359 (3)	C51—C52	1.343 (3)
C5—C6	1.378 (3)	C52—O52	1.317 (2)
C6—N1	1.404 (2)	C51—C56	1.423 (3)
C2—S2	1.754 (2)	C56—O56	1.227 (2)
S2—C21	1.750 (2)		
C4—C5—C57—C51	78.6 (2)	C5—C57—C51—C52	72.9 (2)
C56—C51—C52—C53	3.4 (3)	C52—C51—C56—C55	5.7 (2)
C51—C52—C53—C54	18.6 (3)	C54—C55—C56—C51	−36.1 (2)
C52—C53—C54—C55	−45.3 (2)	C53—C54—C55—C56	54.6 (2)
C52—C53—C54—C541	74.5 (2)	C56—C55—C54—C541	−65.4 (2)
C52—C53—C54—C542	−164.09 (15)	C56—C55—C54—C542	173.8 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
O52—H52···O6	0.84	1.87	2.681 (2)	161
N4—H4A···O56	0.88	2.13	2.952 (2)	155
N4—H4B···O6^{i}	0.88	2.14	2.831 (3)	134

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

Space group $P2_1/n$ was uniquely assigned from the systematic absences. All H atoms were located from difference maps and were thereafter treated as riding atoms, with C—H distances of 0.98 (CH_3) and 0.99 Å (CH_2), N—H distances of 0.88 Å and an O—H distance of 0.84 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants that have provided computing facilities for this work. JC thanks the Ministerio de Educación, Cultura y Deportes, (Programa de Cooperación con Iberoamérica, AECI) of Spain. RA and JQ thank COLCIENCIAS and the Universidad de Valle for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1697). Services for accessing these data are described at the back of the journal.

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