

Data collection: *DIF4* (Stoe & Cie, 1988a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1988b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL* (Sheldrick, 1994). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1099). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,7,9-Trimethyl-2,6-purinedione Monohydrate, C₈H₁₀N₄O₂·H₂O

MASOOD PARVEZ

Department of Chemistry, University of Calgary,
2500 University Drive N.W., Calgary, Alberta,
Canada T2N 1N4

GEORGE FERGUSON

Department of Chemistry and Biochemistry,
University of Guelph, Guelph, Ontario,
Canada N1G 2W1

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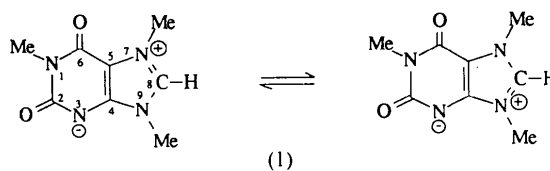
Abstract

The fused-ring system is essentially planar. Both N atoms of the five-membered ring are methylated

with a delocalized positive charge (resulting in a zwitterionic structure, 1,7,9-trimethyl-2,6-dioxo-1,3-dihydropurin-(7/9)-ium-3-ide). One N atom of the six-membered ring is also methylated and the other has a formal negative charge. The crystal contains three types of hydrogen bonding, O—H···O, O—H···N and C—H···O with O···O 2.918 (3), O···N 2.896 (3) and C···O 3.009 (3) Å, and H···acceptor 2.05 (4)–2.06(4) Å.

Comment

The analysis established the structure of the title compound, (1), to be as shown in the scheme below and in Fig. 1. The bond lengths are consistent with a significant contribution from the resonance form shown with a formal negative charge on N(3) and the positive charge in the five-membered ring delocalized over N(7) and N(9), resulting in a zwitterionic structure.



In the six-membered ring, bonds involving N(3) (which has a formal negative charge) are the shortest [N(3)—C(2) 1.351 (3), N(3)—C(4) 1.334 (3) Å] and those involving N(1) are longer [N(1)—C(2) 1.434 (3), N(1)—C(6) 1.391 (3) Å]. The distances involving C(5) [C(4)—C(5) 1.368 (3), C(5)—C(6) 1.421 (3) Å] are also consistent with a major contribution of the ground-state form with C(4)=C(5) a

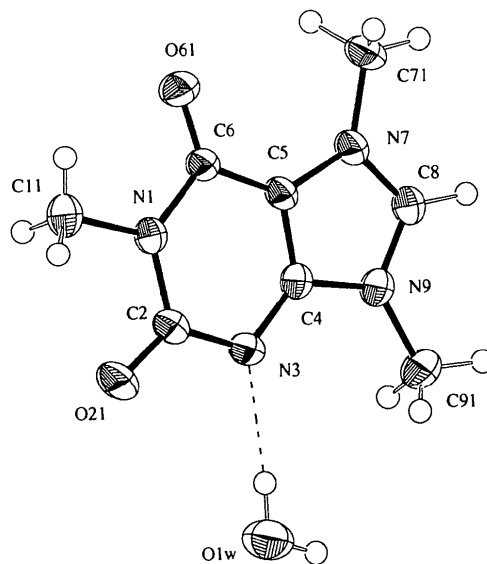


Fig. 1. ORTEP (Johnson, 1976) drawing of the title compound with the crystallographic numbering scheme.

double bond. In the five-membered ring, the distances N(7)—C(8) [1.319 (3) Å] and C(8)—N(9) [1.341 (3) Å] are significantly shorter than C(5)—N(7) [1.389 (3) Å] and C(4)—N(9) [1.387 (3) Å], consistent with a delocalized form involving principally N(7), C(8) and N(9).

The crystal contains three types of hydrogen bonding. The water of hydration is hydrogen bonded to two symmetry-related molecules with hydrogen-acceptor distances (H...A) O(1W)—H(1W)...O(61) 2.06 (4) [O...O 2.918 (3) Å] and O(1W)—H(2W)...N(3) 2.05 (4) Å [O...N 2.896 (3) Å]. Hydrogen bonding is completed by a unique type of C(8)—H(81)...O(21) bond with H...A 2.06 (4) Å [C...O 3.009 (3) Å], between two symmetry-related molecules. The hydrogen bonds do not seem to exert any influence on the water molecule which exhibits a normal 106 (3)° angle. The strongest reflections in the list of structure factors are for the 102 plane and the molecules form hydrogen-bonded sheets in this plane (Fig. 2).

No compound with a similar structure and charge separation appears to have been reported. A search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) revealed data for the following compounds which have a somewhat similar skeleton: caffeine monohydrate (Sutor, 1958*b*), caffeine monohydrate hydrogen triiodide (Herbstein, Kaftory, Kapon & Saenger, 1981), caffeine hydrochloride dihydrate (Mercer & Trotter, 1978), caffeine *m*-nitrobenzoic acid (Martin *et al.*, 1986), caffeine 5-chlorosalicylic acid complex (Shefter, 1968), bis(barbital)-caffeine complex (Craven & Gartland,

1974), isocaffeine (Rasmussen & Sletten, 1973), theophylline monohydrate (Sutor, 1958*a*), theophylline hydrochloride (Koo, Shin & Oh, 1978), theophylline urea (Wiedenfeld & Knoch, 1986) and theophylline *p*-nitrophenol (Aoki, Ichikawa, Koinuma & Iitaka, 1978).

Experimental

Crystal data

C₈H₁₀N₄O₂·H₂O

M_r = 212.2

Monoclinic

*P*2₁/*c*

a = 5.357 (1) Å

b = 17.759 (3) Å

c = 10.251 (1) Å

β = 101.34 (1)°

V = 956.2 (6) Å³

Z = 4

D_x = 1.47 Mg m⁻³

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 10–15°

μ = 0.11 mm⁻¹

T = 293 K

Block

0.40 × 0.25 × 0.25 mm

Colourless

Crystal source: from ethanol

Data collection

Enraf-Nonius CAD-4

diffractometer

ω/2θ scans

Absorption correction:

none

2674 measured reflections

2082 independent reflections

1560 observed reflections

[*I* > 3σ(*I*)]

*R*_{int} = 0.03

θ_{max} = 27°

h = -6 → 6

k = 0 → 22

l = 0 → 13

3 standard reflections

frequency: 120 min

intensity variation: none

Refinement

Refinement on *F*

R = 0.046

wR = 0.049

1560 reflections

174 parameters

Only coordinates of H atoms

refined

w = 1/[σ²(*F*) + 0.0004*F*²]^{1/2}

(Δ/σ)_{max} = 0.03

Δρ_{max} = 0.3 e Å⁻³

Δρ_{min} = -0.3 e Å⁻³

Atomic scattering factors

from Cromer & Mann

(1968) and Stewart,

Davidson & Simpson

(1965)

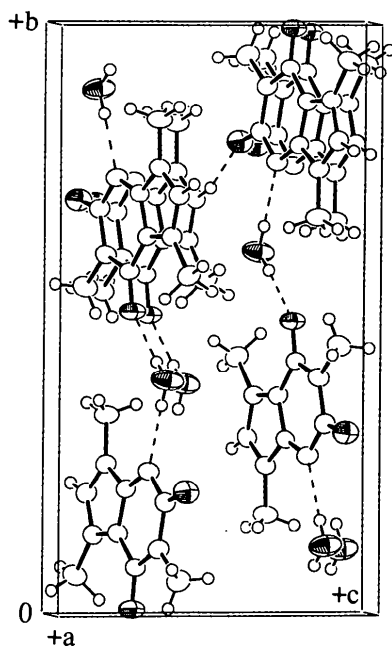


Fig. 2. A view of the unit cell showing intermolecular hydrogen bonding.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
N(1)	0.6895 (3)	0.6064 (1)	0.1553 (2)	0.034 (1)
C(2)	0.7307 (4)	0.6848 (1)	0.1335 (2)	0.036 (1)
N(3)	0.6073 (3)	0.7372 (1)	0.1925 (2)	0.036 (1)
C(4)	0.4575 (4)	0.7092 (1)	0.2703 (2)	0.031 (1)
C(5)	0.4149 (4)	0.6354 (1)	0.2972 (2)	0.032 (1)
C(6)	0.5324 (3)	0.5771 (1)	0.2359 (2)	0.031 (1)
N(7)	0.2428 (3)	0.6338 (1)	0.3823 (2)	0.033 (1)
C(8)	0.1856 (4)	0.7040 (1)	0.4066 (2)	0.035 (1)
N(9)	0.3104 (3)	0.7515 (1)	0.3403 (2)	0.035 (1)
C(11)	0.8237 (5)	0.5526 (1)	0.0853 (3)	0.045 (1)
O(21)	0.8793 (3)	0.7007 (1)	0.0604 (2)	0.052 (1)
O(61)	0.5056 (3)	0.5085 (1)	0.2479 (2)	0.047 (1)
C(71)	0.1484 (5)	0.5671 (1)	0.4420 (2)	0.044 (1)
C(91)	0.2901 (5)	0.8334 (1)	0.3401 (3)	0.047 (1)
O(1W)	0.7413 (4)	0.8889 (1)	0.1286 (3)	0.065 (1)

Table 2. Bond distances (Å), angles (°) and hydrogen-bond geometry (Å, °)

N(1)—C(2)	1.434 (3)	N(1)—C(6)	1.391 (3)
N(1)—C(11)	1.465 (3)	C(2)—N(3)	1.351 (3)
C(2)—O(21)	1.229 (3)	N(3)—C(4)	1.334 (3)
C(4)—C(5)	1.368 (3)	C(4)—N(9)	1.387 (3)
C(5)—C(6)	1.421 (3)	C(5)—N(7)	1.389 (3)
C(6)—O(61)	1.236 (3)	N(7)—C(8)	1.319 (3)
N(7)—C(71)	1.468 (3)	C(8)—N(9)	1.341 (3)
N(9)—C(91)	1.458 (3)		
C(2)—N(1)—C(6)	125.8 (2)	C(2)—N(1)—C(11)	116.8 (2)
C(6)—N(1)—C(11)	117.3 (2)	N(1)—C(2)—N(3)	119.7 (2)
N(1)—C(2)—O(21)	117.1 (2)	N(3)—C(2)—O(21)	123.2 (2)
C(2)—N(3)—C(4)	114.6 (2)	N(3)—C(4)—C(5)	128.4 (2)
N(3)—C(4)—N(9)	125.3 (2)	C(5)—C(4)—N(9)	106.3 (2)
C(4)—C(5)—C(6)	120.2 (2)	C(4)—C(5)—N(7)	107.7 (2)
C(6)—C(5)—N(7)	132.0 (2)	N(1)—C(6)—C(5)	111.3 (2)
N(1)—C(6)—O(61)	121.6 (2)	C(5)—C(6)—O(61)	127.2 (2)
C(5)—N(7)—C(8)	107.9 (2)	C(5)—N(7)—C(71)	127.2 (2)
C(8)—N(7)—C(71)	124.9 (2)	N(7)—C(8)—N(9)	110.0 (2)
C(4)—N(9)—C(8)	108.2 (2)	C(4)—N(9)—C(91)	126.1 (2)
C(8)—N(9)—C(91)	125.7 (2)		
D—H...A	H...A	D...A	D—H...A
O(1W)—H...N(3)	2.05 (4)	2.896 (3)	174 (3)
O(1W)—H...O(61 ^h)	2.06 (4)	2.918 (3)	173 (3)
C(8)—H...O(21 ^h)	2.06 (4)	3.009 (3)	156 (3)

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

Space group $P2_1/c$ was determined from systematic absences ($0k0$, k odd; $h0l$, l odd). Corrections for Lorentz-polarization effects were applied. The structure was solved by direct methods using *MULTAN80* (Main *et al.*, 1980) and refined by full-matrix least-squares calculations. Non-H atoms were allowed to refine with anisotropic displacement parameters. H-atoms were allowed to refine with overall isotropic displacement parameters. Other computer programs used include *SHELX76* (Sheldrick, 1976) and *XANADU* (Roberts & Sheldrick, 1975).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BR1053). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Fluorinated Barbituric Acid Derivatives

DARRYL D. DESMARTEAU AND
WILLIAM T. PENNINGTON

*Department of Chemistry, Clemson University,
Clemson, South Carolina 29634-1905, USA*

GIUSEPPE RESNATI

*CNR, Centro di Studio delle Sostanze Organiche
Naturali, Dipartimento di Chimica del Politecnico,
Piazza L. da Vinci 32, I-20133 Milan, Italy*

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Abstract

The structures of 5,5-difluorobarbituric acid, $C_4H_2F_2N_2O_3$ (1), and 5-fluoro-5-phenylbarbituric acid, $C_{10}H_7FN_2O_3$ (2), have been determined [barbituric acid is 2,4,6(1*H*,3*H*,5*H*)-pyrimidinetrione]. Both compounds have the expected keto structure. The C—C bonds in the heterocyclic ring [1.526 (8) Å for (1), 1.525 (6) and 1.537 (6) Å for (2)] are elongated relative to those of the parent compounds, consistent with the electron-withdrawing power of the F-atom substituent(s). There is extensive intermolecular hydrogen bonding in both compounds.

Comment

Selective fluorination of biologically active compounds often induces useful pharmacological proper-