Table 5. *Short interatomic distances (Å) for (2) and (3)*

(2)			
S1···S6^{i}	3.385 (1)	S6···S7^{ii}	3.780 (1)
S2···S6^{i}	3.407 (1)		
(3)			
S2···S6^{iii}	3.384 (1)	S6···S7^{v}	3.786 (1)
S1···S6^{iii}	3.422 (1)	S1···S6^{vi}	3.906 (1)
S6···S7^{iv}	3.683 (1)	S2···S2^{iii}	3.928 (1)
S1···S7^{v}	3.746 (1)		

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

The structures were solved by direct methods and completed through successive cycles of ΔF synthesis (including all of the H atoms). Anisotropic displacement parameters were used for non-H atoms, while an isotropic riding model was used for H atoms.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structures: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997*b*); molecular graphics: *XP* (*SHELXTL/PC*; Sheldrick, 1994); software used to prepare material for publication: *PARST* (Nardelli, 1983). Literature search: CSD (Allen & Kennard, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1396). Services for accessing these data are described at the back of the journal.

References

Aimar, M. L. & de Rossi, R. H. (1996). *Tetrahedron Lett.* **37**, 2137–2140.

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Baggio, R., Vega, D., Aimar, M., de Rossi, R. H. & Ellena, J. (1997). *Acta Cryst.* C**53**, 1125–1127.

Lu, F. L., Keshavarz-K, M., Srdanov, G., Jacobson, R. H. & Wudl, F. (1989). *J. Org. Chem.* **54**, 2165–2169.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1994). *SHELXTL/PC*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997*a*). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Wei, C. H. (1983). *Acta Cryst.* C**39**, 1079–1082.

Wei, C. H. (1985). *Acta Cryst.* C**41**, 1768–1770.

Wei, C. H. (1986). *Acta Cryst.* C**42**, 1836–1839.

Acta Cryst. (1998). C**54**, 1905–1907

Thiabendazolium Nitrate, an Anthelmintic Compound

SOMASUNDARAM MURUGESAN, PONRAJ PRABAKARAN AND PACKIANATHAN THOMAS MUTHIAH*

Department of Chemistry, Bharathidasan University, Tiruchirapalli 620024, Tamilnadu, India. E-mail: tomm@bdu.ernet.in

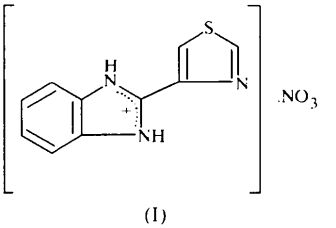
(*Received 23 February 1998; accepted 30 June 1998*)

Abstract

In the crystal structure of 2-(thiazol-4-yl)-1*H*-benzimidazolium nitrate, $C_{10}H_8N_3S^+.NO_3^-$, the benzimidazole moiety is protonated. The benzimidazole and thiazole systems are coplanar. Both N—H groups of the protonated benzimidazole are involved in N—H···O hydrogen bonds with the nitrate anion.

Comment

Substituted benzimidazoles show antiviral action and anthelmintic activity. This has been attributed to their metal-chelating ability (Margaret *et al.*, 1985). Thiabendazole [2-(thiazol-4-yl)-1*H*-benzimidazole] is a broad-spectrum anthelmintic compound useful in the treatment of parasitic diseases of humans and animals. It is also useful as a fungicide for spoilage control of citrus fruit (Windholz, 1983). In its metal-chelating behaviour, it is similar to both 2,2′-bipyridine and 1,10-phenanthroline. The crystal structure of thiabendazole (Trus & Marsh, 1973), and its complexes with cobalt (Kowala & Wunderlich, 1973; Umadevi *et al.*, 1995), copper (Udupa & Krebs, 1979) and platinum (Rong *et al.*, 1991) have been reported. This paper deals with the crystal structure of a protonated thiabendazole moiety, namely, thiabendazolium nitrate, (I).



(I)

The N atom of the benzimidazole moiety rather than that of the thiazole group is protonated. This protonation leads to equalization of the bond angles at the two N atoms of the benzimidazole group, in contrast to the benzimidazole group in the crystal structure of free thiabendazole where the two bond angles are different (Trus & Marsh, 1973). The C—C bond connecting the two

ring systems [1.447 (4) Å] is of the same length, within experimental error, as that in neutral thiabendazole [1.442 (10) Å]. This value suggests appreciable delocalization across this bond (Trus & Marsh, 1973). The benzimidazole and thiazole systems are coplanar, the dihedral angle between them being 0.44 (12)°. The corresponding angle is 10° in free thiabendazole (Trus & Marsh, 1973) and 8.9 (1)° in thiabendazole hydrobromide dihydrate (Pannerselvam & Thomas Muthiah, 1998). In the metal complexes, these values are as follows: 4.85 (17) and 4.34 (11)° in a cobalt bis-complex (Kowala & Wunderlich, 1973), 1.71 (2) and 3.95 (3)° in a second cobalt bis-complex (Umadevi *et al.*, 1995), and 9.81 (14) and 7.91 (3)° in a copper bis-complex (Udupa & Krebs, 1979). These values indicate that neutral thiabendazole, the thiabendazole cation and the complexed thiabendazole ligand maintain a near coplanar geometry. The thiabendazole cation is involved in a pair of N—H···O hydrogen bonds [N1···O16^{i} 2.863 (3) Å and N1—H1···O16^{i} 171 (3)°; N3···O17 2.805 (3) Å and N3—H3···O17 171 (3)°; symmetry code: (i) $x-\frac{1}{2}$, $\frac{3}{2}-y$, $z-\frac{1}{2}$].

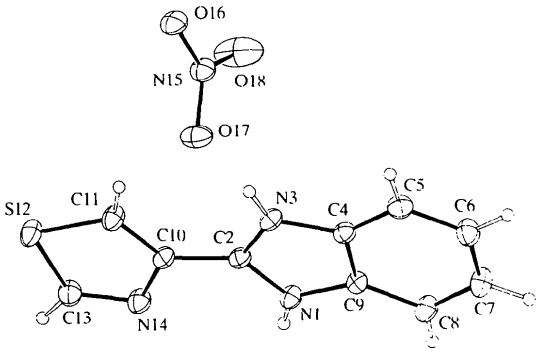


Fig. 1. An *ORTEP*II (Johnson, 1976) view of the title molecule with displacement ellipsoids at the 40% probability level.

Experimental

Thiabendazole (obtained from Merck, Sharp & Dohme) was dissolved in methanol. The solution was acidified with dilute nitric acid. Pale-yellow needle-shaped crystals appeared after a few days.

Crystal data

$C_{10}H_8N_3S^+.NO_3^-$
M_r = 264.26
Monoclinic
$P2_1/n$
a = 4.8509 (15) Å
b = 14.0214 (12) Å
c = 16.671 (3) Å
β = 97.43 (2)°
V = 1124.4 (4) Å^3
Z = 4
D_x = 1.561 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71070 Å
Cell parameters from 25 reflections
θ = 2–25°
μ = 0.29 mm^{-1}
T = 293 (2) K
Needle
0.40 × 0.15 × 0.12 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2220 measured reflections
1973 independent reflections
1634 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 24.97°
$h = 0 \rightarrow 5$
$k = 0 \rightarrow 16$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: negligible

Refinement

Refinement on F^2
$R(F)$ = 0.049
$wR(F^2)$ = 0.122
S = 1.213
1973 reflections
195 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0399P)^2 + 1.0604P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.468 e Å^{-3}
$\Delta\rho_{min}$ = −0.336 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S12—C11	1.700 (3)	N14—C10	1.372 (4)
S12—C13	1.710 (3)	N14—C13	1.300 (4)
N1—C2	1.334 (4)	O16—N15	1.244 (3)
N1—C9	1.391 (4)	O17—N15	1.242 (4)
N3—C2	1.333 (4)	O18—N15	1.216 (5)
N3—C4	1.382 (4)		
C11—S12—C13	88.92 (16)	N1—C9—C4	106.6 (3)
C2—N1—C9	108.6 (2)	N1—C9—C8	131.5 (3)
C2—N3—C4	109.4 (2)	N14—C10—C2	119.2 (3)
C10—N14—C13	109.1 (3)	N14—C10—C11	116.0 (3)
N1—C2—N3	109.1 (2)	S12—C11—C10	110.1 (2)
N1—C2—C10	125.6 (3)	S12—C13—N14	115.9 (2)
N3—C2—C10	125.2 (3)	O16—N15—O17	120.7 (3)
N3—C4—C5	132.3 (3)	O16—N15—O18	121.1 (3)
N3—C4—C9	106.2 (2)	O17—N15—O18	118.2 (3)

H atoms were located from a difference Fourier map and their coordinates and isotropic displacement parameters were refined.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

SM, PP and PTM acknowledge UGC, India, for a Junior Research Fellowship, a Project Assistantship and a Career Award, respectively. The authors thank RSIC–IIT, Madras (a DST-funded facility, Government of India), for X-ray data collection, and Merck, Sharp & Dohme Inc. (USA) for a sample of the drug.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1084). Services for accessing these data are described at the back of the journal.

References

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kowala, C. & Wunderlich, J. A. (1973). *Inorg. Chim. Acta*, **7**, 331–338.
Margaret, G., Steven, D. H., Brain, P. & David, J. W. (1985). *Inorg. Chim. Acta*, **107**, 49–55.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Pannerselvam, P. & Thomas Muthiah, P. (1998). In preparation.
Rong, M., Muir, M. M., Cadiz, M. E. & Muir, J. A. (1991). *Acta Cryst.* C**49**, 1539–1541.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Trus, B. L. & Marsh, R. E. (1973). *Acta Cryst.* B**29**, 2298–2301.
Udupa, M. R. & Krebs, B. (1979). *Inorg. Chim. Acta*, **32**, 1–5.
Umadevi, B., Thomas Muthiah, P., Shui, X. & Eggleston, D. S. (1995). *Inorg. Chim. Acta*, **234**, 149–152.
Windholz, M. (1983). Editor. *The Merck Index*, 10th ed. Rahway, NJ, USA: Merck & Co. Inc.

Acta Cryst. (1998). C**54**, 1907–1909

9-(Carboxymethyl)-6-chloropurine Ethyl Ester†

GEETA SOOD, CARL H. SCHWALBE AND WILLIAM FRASER

Pharmaceutical Sciences Institute, Aston University, Aston Triangle, Birmingham B4 7ET, England. E-mail: c.h.schwalbe@aston.ac.uk

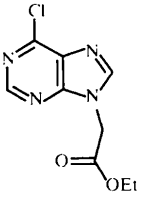
(Received 6 May 1998; accepted 8 July 1998)

Abstract

Alkylation of 6-chloropurine using ethyl bromoacetate gives a mixture of monoalkyl regio-isomers from which the title compound, $C_9H_9ClN_4O_2$, was isolated in crystalline form. In both independent molecules, the side chain adopts an extended conformation; its carboxymethyl-group plane intersects the planar heterocycle at angles of 60.1 (1) and 65.8 (1)°, respectively.

Comment

The synthetic usefulness of *N*-substituted chloropurines is well documented; displacement of the chloro group can be achieved using amine or oxygen nucleophiles to provide adenine and hypoxanthine analogues with defined substitution patterns. This route, particularly to substituted hypoxanthines, is preferred (Rao & Revankar, 1995) since direct alkylation of hypoxanthine itself gives mixtures containing peralkylated products (Sood *et al.*, 1998*a*). Although direct alkylation of 6-chloropurine attaches a substituent at either N9 or N7, alkylation occurs predominantly at N9 in the absence of protecting groups (Dalby *et al.*, 1993). The distribution of regio-isomers is similar, whether potassium carbonate (Sood *et al.*, 1998*c*) or sodium hydride (Rao & Revankar, 1995) is used as the base. Alkylation of 6-chloropurine using ethyl bromoacetate gave a separable mixture of crystalline regio-isomeric products: 7-(carboxymethyl)-6-chloropurine ethyl ester, (II), in 27% yield, and the title compound, (I), in 65% yield. Although we have already reported on the crystal structure of (II) (Sood *et al.*, 1998*c*), only recently did we obtain X-ray diffraction quality crystals of its regio-isomer, (I). We decided to determine the crystal structure of (I) in order to illustrate that the ethyl acetate side chain was indeed attached at N9 as anticipated, and also to compare the structure of (I) with its regio-isomer, (II), and related structures.



(I)

Two molecules, (I*A*) and (I*B*), constitute the asymmetric unit. The ethyl acetate side chain in (I) avoids steric hindrance with the heterocycle by emerging from N9 with the C8—N9—C10—C11 torsion angle equal to 58.2 (5)° in (I*A*) and 65.1 (5)° in (I*B*). In the reported series of substituted analogues containing the same ethyl acetate fragment (Sood *et al.*, 1997*b*; Flensburg & Egholm, 1994) or the methyl homologue (Sood *et al.*, 1997*a*, 1998*b*), the equivalent torsion angle ranges are 50.8 (6) to 104.65 (13) and −92.9 (3) to −104.5 (2)°, respectively. The ring atoms in (I*A*) and (I*B*) are planar, with r.m.s. deviations of 0.006 and 0.009 Å, respectively. Many of the geometrical features of (I) resemble those of its 2,6-dichloro analogue (Chan *et al.*, 1995), but with the internal N3—C2—N1 angle in (I) marginally compressed, by 1.8 (4)°. Compared with the regio-isomer, (II), attachment of the substituent at N9 expands the internal angles at C5 by 4.3 (4) and at N9 by 1.8 (4)°, whereas C4 and N7 are contracted by −4.2 (4) and −1.5 (4)°. The side chain in (I) differs from (II), both in its relationship to the heterocycle and in its conformation; torsion angles for (I*A*) and (I*B*) are given in Table 1, and show an almost fully extended conformation. In the absence of any amino groups, the most significant of several C—H···O contacts is a weak hydrogen bond between H8*A* and a nearby O12*B* carbonyl group in the other independent molecule in the unit cell, with H8*A*···O12*B*^{i} = 2.52 (2) Å [symmetry code: (i) $-x+1, -y, -z+1$].

† Alternative name: ethyl 6-chloropurine-9-acetate.