Acta Cryst. (1984). C**40**, 1724–1726

Methyl 2(2*H*)-Oxopyrimido[2,1-*b*][1,3]benzothiazole-4-acetate, $C_{13}H_{10}N_2O_3S$

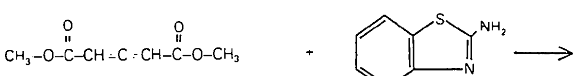
By S. B. Sanni,* M. De Wolf and A. T. H. Lenstra†

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, *B*-2610 *Wilrijk, Belgium*

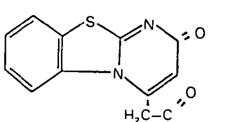
(*Received* 11 *April* 1984; *accepted* 30 *May* 1984)

Abstract. $M_r = 274.3$, monoclinic, $P2_1/n$, $a = 9.593$ (4), $b = 9.213$ (5), $c = 13.745$ (6) Å, $\beta = 107.89$ (2)°, $Z = 4$, $V = 1156.0$ Å^3, $F(000) = 568$, $D_x = 1.576$ Mg m^{-3}, Mo radiation, $\lambda = 0.71073$ Å, $\mu = 0.285$ mm^{-1}, $R = 0.035$, $R_w = 0.034$ for 1773 reflections with $I > 2\sigma(I)$ out of 2028 independent measurements at room temperature. The molecule consists of a slightly warped ring skeleton, in which the thiazole ring approaches an envelope form, the pyrimido ring a twist-boat and the benzo ring a true-boat conformation. The variations of bond lengths and angles reflect the conflicting angular demands placed upon the system by the individual components.

Introduction. Reaction of dimethyl 2,3-pentadienedioate (I) with 2-amino-1,3-benzothiazole (II) following a procedure outlined by Chan, Ma & Mak (1977) results in the title compound (III) m.p. 496–498 K. Although each separate ring in (III) is rather rigid the fusion brings together a large number of conflicting demands, particularly in the valence angles. The X-ray analysis was undertaken to investigate the response of the molecule to these demands. The results should confirm and extend the observations of Chan, Ma & Mak (1977) who found a slight warping of the ring system in the similar methyl 2(2*H*)-oxopyrimido[2,1-*b*][1,3]benzothiazole-4-carboxylate.



(I) (II)



(III)

Experimental. Suitable single crystals obtained by recrystallization from methanol/dimethylformamide. Unit-cell dimensions deduced from 25 high-order reflections. Enraf–Nonius CAD-4 diffractometer, ω/θ scan, Mo radiation monochromatized by pyrolitic graphite. Max. Bragg angle 25°. 2028 independent measurements, 1773 considered observed $[I > 2\sigma(I)]$. $0 \le h \le 11$, $0 \le k \le 10$, $-16 \le l \le 15$. Intensity control showed no drift. Space group inferred from systematic extinctions ($0k0$ with $k = 2n+1$, $h0l$ with $h+l = 2n+1$) (equivalent positions: x, y, z; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; $-x, -y, -z$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$). No absorption correction in view of the size of the crystal (0·2 × 0·2 × 0·15 mm) and the low value of μ. Using *MULTAN* (Germain, Main & Woolfson, 1971), the most likely *E* map with 251 terms showed all non-hydrogen atoms. H-atom positions found subsequently from a difference electron density map. Least-squares refinement (on *F*'s) of all positional parameters, but with the Debye–Waller temperature factor for H atoms fixed at 4 Å^2 (overall *B* from Wilson plot 3 Å^2). Reflections given individual weights based on counting statistics. Convergence reached at $R = 0.045$, $R_w = 0.065$. From the F_o/F_c listing it was clear that extinction could not be neglected; refinement of the extinction parameter to 2.55×10^{-6} (Zachariasen, 1963) resulted in $R = 0.035$ and $R_w = 0.034$. $(\Delta/\sigma)_{max} = 0.05$. Max. noise level in final difference Fourier map 0·1 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius *SDP* computer programs (Frenz, 1978) were employed.

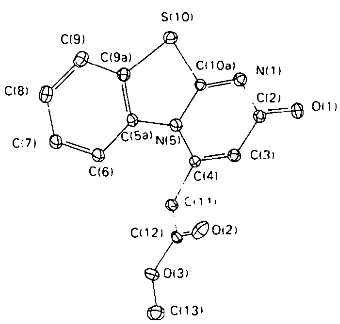


Fig. 1. Structural formula, conformation and atomic numbering scheme of the title compound.

* On leave, from the University of Benin, Benin City, Nigeria.
† Author to whom correspondence should be addressed.

0108-2701/84/101724-03$01.50

Table 1. *Positional parameters in fractions of the cell edges and isotropic thermal parameters*

The e.s.d.'s given in parentheses refer to the last digit. Isotropic temperature parameters ($Å^2$) are calculated from anisotropic temperature parameters assuming equal volume of the 50% probability region according to Lipson & Cochran (1968): $B_{iso} - 8\pi^2(U^o_{11}U^o_{22}U^o_{33})^{1/3}$. All anisotropic thermal parameters were physically acceptable.

	x	y	z	B_{iso}
N(1)	−0·1215 (2)	0·0585 (2)	−0·2258 (1)	2·59
C(2)	−0·1811 (2)	−0·0721 (2)	−0·2664 (1)	2·68
C(3)	−0·1098 (2)	−0·2022 (2)	−0·2154 (1)	2·57
C(4)	0·0169 (2)	−0·1991 (2)	−0·1386 (1)	2·16
N(5)	0·0782 (2)	−0·0637 (2)	−0·1044 (1)	2·09
C(5a)	0·2092 (2)	−0·0264 (2)	−0·0250 (1)	2·11
C(6)	0·3187 (2)	−0·1147 (2)	0·0338 (2)	2·85
C(7)	0·4356 (2)	−0·0519 (2)	0·1067 (2)	3·02
C(8)	0·4436 (2)	0·0949 (3)	0·1239 (2)	3·11
C(9)	0·3351 (2)	0·1855 (2)	0·0660 (2)	3·08
C(9a)	0·2199 (2)	0·1234 (2)	−0·0099 (1)	2·50
S(10)	0·07582 (6)	0·21770 (6)	−0·09319 (4)	2·91
C(10a)	−0·0022 (2)	0·0569 (2)	−0·1495 (1)	2·30
O(1)	−0·2894 (2)	−0·0748 (2)	−0·3431 (1)	3·60
C(11)	0·0889 (2)	−0·3378 (2)	−0·0925 (1)	2·44
C(12)	0·2117 (2)	−0·3798 (2)	−0·1335 (1)	2·27
O(2)	0·2416 (2)	−0·3209 (2)	−0·2015 (1)	3·70
O(3)	0·2824 (1)	−0·4956 (2)	−0·0845 (1)	3·04
C(13)	0·3926 (2)	−0·5547 (3)	−0·1245 (2)	3·72

Table 2. *Bond lengths* (Å) *and valence angles* (°) *of the title compound and the corresponding 4-carboxylate* (*Chan et al.*, 1977), *with e.s.d.'s in parentheses*

	This work	Chan *et al.* (1977)		This work	Chan *et al.* (1977)
N(1)–C(2)	1·375 (1)	1·348 (8)	C(6)–C(7)	1·380 (1)	1·373 (8)
N(1)–C(10a)	1·293 (1)	1·294 (7)	C(7) C(8)	1·370 (1)	1·388 (9)
C(2)–C(3)	1·449 (1)	1·475 (9)	C(8)–C(9)	1·380 (1)	1·375 (9)
C(2)=O(1)	1·233 (1)	1·230 (8)	C(9)–C(9a)	1·389 (1)	1·391 (8)
C(3)–C(4)	1·343 (1)	1·344 (8)	C(9a)–S(10)	1·733 (1)	1·753 (5)
C(4)–N(5)	1·397 (1)	1·380 (6)	S(10)–C(10a)	1·732 (1)	1·737 (6)
C(4)–C(11)	1·498 (1)	1·514	C(11)–C(12)	1·505 (1)	—
N(5)–C(5a)	1·431 (1)	1·434 (6)	C(12)=O(2)	1·190 (1)	1·187 (7)
N(5)–C(10a)	1·386 (1)	1·387 (7)	C(12)–O(3)	1·330 (1)	1·332 (7)
C(5a)–C(6)	1·378 (1)	1·377 (7)	C(13)–O(3)	1·441 (1)	1·474 (7)
C(5a)–C(9a)	1·394 (1)	1·408 (8)			
C(2)–N(1)–C(10a)	118·2 (1)	118·5 (5)	C(6)–C(7)–C(8)	121·9 (1)	121·9 (5)
N(1)–C(2)–C(3)	116·9 (1)	116·8 (5)	C(7)–C(8)–C(9)	120·3 (1)	120·8 (6)
N(1)–C(2)–O(1)	120·1 (1)	121·6 (6)	C(8)–C(9)–C(9a)	118·0 (1)	117·7 (6)
C(3)–C(2)–O(1)	123·1 (1)	121·6 (6)	C(5a)–C(9a)–C(9)	121·7 (1)	121·3 (5)
C(2)–C(3)–C(4)	122·8 (1)	121·0 (5)	C(5a)–C(9a)–S(10)	113·0 (1)	112·3 (4)
C(3)–C(4)–N(5)	117·9 (1)	119·7 (5)	C(9)–C(9a)–S(10)	125·4 (1)	126·3 (4)
C(3)–C(4)–C(11)	120·2 (1)	119·5 (5)	C(9a)–S(10)–C(10a)	90·8 (1)	91·2 (3)
N(5)–C(4)–C(11)	121·9 (1)	119·6 (4)	S(10)–C(10a)–N(5)	112·4 (1)	111·8 (4)
C(4)–N(5)–C(10a)	116·5 (1)	116·6 (4)	S(10)–C(10a)–N(1)	120·4 (1)	121·2 (4)
C(4)–N(5)–C(5a)	130·7 (1)	129·4 (4)	N(1)–C(10a)–N(5)	127·2 (1)	127·1 (5)
C(5a)–N(5)–C(10a)	112·7 (1)	113·9 (4)	C(4)–C(11)–C(12)	111·9 (1)	—
N(5)–C(5a)–C(9a)	110·0 (1)	110·6 (4)	C(11)–C(12)–O(2)	125·6 (1)	122·6 (5)
N(5)–C(5a)–C(6)	129·7 (1)	129·4 (5)	C(11)–C(12)–O(3)	110·6 (1)	111·3 (4)
C(6)–C(5a)–C(9a)	119·3 (1)	119·9 (5)	O(2)–C(12)–O(3)	123·8 (1)	126·0 (5)
C(5a)–C(6)–C(7)	118·7 (1)	118·3 (5)	C(12)–O(3)–C(13)	115·4 (1)	114·9 (5)

Discussion. Refined atomic coordinates are listed in Table 1,* with the numbering scheme of the atoms presented in Fig. 1. Table 2 gives interatomic distances and angles both of the title compound and of the corresponding 4-carboxylate (Chan, Ma & Mak, 1977). The comparison reveals an excellent agreement, better than could be expected in view of the carboxylate structure being solved from photographic data to $R = 0{\cdot}099$. Apart from a few differences in the ester groupings, the only significant discrepancy is that the C—S bonds in the title compound have equal lengths, whereas they were observed to be different in the 4-carboxylate. Nevertheless, in both compounds the C—S bonds have values intermediate between those accepted for a single (1·808 Å) and a double bond (1·556 Å) proving that the **S** lone pairs participate in the electronic bonding scheme. The bond C(10a)—N(1) has a length (1·294 Å) characteristic of CN double bonds. In contrast, other C—N bonded distances are intermediate between single and double CN bonds. The value of 1·431 Å for N(5)—C(5a) is somewhat special. It is elongated because of the angular strain introduced in the molecule by bringing together conflicting angular demands. The 'quinonoid' character of the pyrimido ring is clearly seen from the short C(10a)—N(1) and C(3)—C(4) bonds as well as from the distribution of valence angles

* Lists of structure factors, H-atom positions and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39543 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Endocyclic torsion angles* (°) *and Cremer & Pople* (1975) *ring-puckering parameters, e.s.d.'s on the latter calculated according to Norrestam* (1981)

C(5a)–C(9a)–S(10)–C(10a)	0·3 (2)	$Q = 0{\cdot}021$ (3) Å
C(9a)–S(10)–C(10a)–N(5)	1·2 (2)	$\varphi = 257$ (8)°
S(10)–C(10a)–N(5)–C(5a)	−2·4 (2)	Numbering sequence:
C(10a)–N(5)–C(5a)–C(9a)	2·6 (2)	S(10),C(10a),N(5),C(5a),C(9a)
N(5)–C(5a)–C(9a)–S(10)	−1·7 (2)	
C(10a)–N(1)–C(2)–C(3)	4·0 (2)	$q_2 = 0{\cdot}068$ (4), $q_3 = -0{\cdot}003$ (4) Å
N(1)–C(2)–C(3)–C(4)	−6·7 (2)	$Q = 0{\cdot}068$ (4) Å
C(2)–C(3)–C(4)–N(5)	2·7 (2)	$\theta = 93$ (3)°
C(3)–C(4)–N(5)–C(10a)	3·4 (2)	$\varphi = 260$ (3)°
C(4)–N(5)–C(10a)–N(1)	−6·4 (2)	Numbering sequence:
N(5)–C(10a)–N(1)–C(2)	2·4 (2)	N(1),C(2),C(3),C(4),N(5),C(10a)
C(8)–C(9)–C(9a)–C(5a)	2·9 (2)	$q_2 = 0{\cdot}027$ (4), $q_3 = -0{\cdot}005$ (4) Å
C(9)–C(9a)–C(5a)–C(6)	−2·8 (2)	$Q = 0{\cdot}028$ (4) Å
C(9a)–C(5a)–C(6)–C(7)	0·4 (2)	$\theta = 100$ (8)°
C(5a)–C(6)–C(7)–C(8)	1·8 (2)	$\varphi = 237$ (9)°
C(6)–C(7)–C(8)–C(9)	−1·7 (2)	Numbering sequence:
C(7)–C(8)–C(9)–C(9a)	−0·7 (2)	C(9),C(9a),C(5a),C(6),C(7),C(8)

in this ring. These observations confirm the conclusions drawn by Chan, Ma & Mak (1977).

Furthermore, we note a slightly elongated C(5a)—C(9a) bond and a distinct warping of all rings, again resulting from the angular strain in the polycyclic system. Endocyclic torsion angles, presented in Table 3, show small but significant deviations from planarity, while Cremer & Pople (1975) parameters indicate the shape adopted by each individual ring. The central thiazole ring is near to an envelope conformation with the (pseudo-)mirror plane passing through N(5) and the middle of the C(9a)—S bond. In the notation of Boeyens (1978), the pyrimido ring approaches a $^2T_6$ form, *i.e.* a twist-boat conformation with a (pseudo-)twofold axis through N(1) and C(4), while the benzo ring is near to a $^{2,5}B$ form, *i.e.* a true-boat conformation with C(7) and C(9a) as bowsprits. The distortion of an aromatic ring into a boat form rather than into a chair form is in keeping with force-constant calculations of Pulay, Fogarasi & Boggs (1981). Our present observation of the boat form adopted by a benzene moiety corroborates previous results (Lenstra & Petit, 1980; Van Havere, Lenstra & Geise, 1982; Van Havere, Lenstra, Geise, Van den Berg & Benschop, 1982) in sterically demanding situations created by substitutions on aromatic nuclei.

Finally, the planar carboxy group C(11),C(12),-O(2),O(3) is almost perpendicular to the 'plane' of the pyrimido ring.

The authors wish to thank Mrs Dorcas Okor, who in cooperation with Dr F. Scheinmann (Salford University, England) prepared the title compound. Partial financial assistance to SBS by the University of Benin is gratefully acknowledged.

References

BOEYENS, J. C. A. (1978). *J. Cryst. Mol. Struct.* **8**, 317–320.
CHAN, C., MA, J. C. N. & MAK, T. C. W. (1977). *J. Chem. Soc. Perkin Trans.* 2, pp. 1070–1074.
CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
FRENZ, B. A. (1978). *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 64–71. Delft Univ. Press.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
LENSTRA, A. T. H. & PETIT, G. H. (1980). *Cryst. Struct. Commun.* **9**, 725–730.
LIPSON, H. & COCHRAN, W. (1968). *The Determination of Crystal Structures*, pp. 301 ff. London: Bell.
NORRESTAM, P. (1981). *Acta Cryst.* A**37**, 764–765.
PULAY, P., FOGARASI, G. & BOGGS, J. E. (1981). *J. Chem. Phys.* **74**, 3999–4014.
VAN HAVERE, W., LENSTRA, A. T. H. & GEISE, H. J. (1982). *Acta Cryst.* B**38**, 3119–3120.
VAN HAVERE, W., LENSTRA, A. T. H., GEISE, H. J., VAN DEN BERG, G. R. & BENSCHOP, H. P. (1982). *Acta Cryst.* B**38**, 1635–1637.
ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1984). C**40**, 1726–1728

Structure of Salicin, $C_{13}H_{18}O_7$

BY KATSUHIKO UENO

Research Institute for Polymers and Textiles, Yatabe-Higashi 1-1-4, *Tsukuba Ibaraki* 305, *Japan*

(*Received* 5 *March* 1984; *accepted* 30 *May* 1984)

Abstract. $M_r = 286\cdot3$, orthorhombic, $P2_12_12_1$, $a = 8\cdot314\,(1)$, $b = 21\cdot169\,(3)$, $c = 7\cdot650\,(1)$ Å, $U = 1346\cdot4\,(3)$ Å^3, $D_m = 1\cdot41$, $D_x = 1\cdot41$ Mg m^{-3}, $Z = 4$, $\lambda(\text{Cu } K\alpha) = 1\cdot5418$ Å, $\mu(\text{Cu } K\alpha) = 1\cdot12$ mm^{-1}, $F(000) = 608$, $T = 298$ K, $R = 0\cdot038$ for 1552 observed reflexions. The torsion angle around the glucosidic C—O bond is 14·6 (4)°. The bond angle at the glucosidic O atom is 117·8 (2)°. The molecules are linked *via* hydrogen bonding to form strings along the twofold screw axes parallel to **a** and **c**.

Introduction. It has been proposed that the orientation of glucosyl bonds in dihydroxycoumarin β-glucoside be classified into two characteristic conformations: 'in-plane' and 'out-of-plane' with respect to the aromatic plane (Ueno, Shiraki, Sato & Saito, 1985). The in-plane conformation is commonly observed in other β-glucosides and even in the aromatic α-glucosides (Swaminathan, 1982). Although these structures result in considerable intramolecular repulsions, the repulsive energy is considered to be compensated by the resonance of π electrons of the glucosidic O atoms with the aromatic ring. The out-of-plane conformation, on the other hand, has neither of the above factors and is observed in 8-glucosyloxy-7-hydroxycoumarin (Ueno, Saito & Sato, 1978). Salicin [2-(hydroxymethyl)phenyl β-D-glucopyranoside], which is usually obtained from the bark of poplar and willow and has been used as an analgesic, has a glucosidic linkage to an aromatic ring with a bulky substituent, a $-CH_2OH$ group, at its *ortho* position. The present paper deals with the structure of salicin in order to examine further details of the conformation of glucosyl bonds.

Experimental. Prismatic crystals from aqueous ethanol solution. Crystal 0·26 × 0·22 × 0·40 mm. D_m by flotation in a mixture of dichloromethane and chloroform. Nicolet *P*3/*F* automated four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation. Unit-cell dimensions by least squares with 2θ values of 25 reflexions. Systematic absences $h00$, h odd, $0k0$, k odd, $00l$, l odd. Intensity data $4° < 2\theta < 150°$. $\omega/2\theta$

0108-2701/84/101726-03$01.50