Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

Sodium *p*-nitrobenzoxasulfamate monohydrate

Turan K. Yazicilar,[a] Omer Andac,[a] Yunus Bekdemir,[a] Halil Kutuk,[a] Veysel T. Yilmaz[a]* and William T. A. Harrison[b]

[a]Department of Chemistry, Faculty of Arts and Science, Ondokuz Mayıs University, 55139 Kurupelit Samsun, Turkey, and [b]Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland
Correspondence e-mail: vtyilmaz@omu.edu.tr

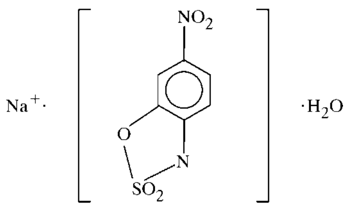
Received 5 July 2001
Accepted 22 October 2001
Online 14 December 2001

The title compound, alternatively named sodium 6-nitro-3*H*-1,2,3-benzoxathiazole 2,2-dioxide monohydrate, $Na^+\cdot C_6H_3N_2O_5S^-\cdot H_2O$, consists of chains of NaO_7 units, with the seven donor-O atoms coming from two water molecules and five *p*-nitrobenzoxasulfamate anions. The seven-coordinate geometry around the Na^+ ion is described as monocapped trigonal prismatic, but with a large distortion from ideal geometry. Each triangular face is defined by one O atom each from a water molecule, a nitro group and a sulfonyl group. An O atom from a sulfonyl group caps one of the square faces of the trigonal prism in an unsymmetrical fashion. The water molecules and one sulfonyl O atom are involved in bridging adjacent units, as is the nitro group of the anion. The sulfamate ions adopt an antiparallel alignment between the NaO_7 units and are connected to each other by C—H···O and π–π interactions. The three-dimensional crystal structure is stabilized by a network of strong O—H···N hydrogen bonds.

Comment

Sulfamate derivatives have considerable commercial importance as artificial sweeteners (Spillane *et al.*, 1996; Drew *et al.*, 1998). The structures of acyclic sulfamate $(NH_2SO_3)^-$ salts of lithium (Stade *et al.*, 2001), rubidium (Schreuer, 1999*a*) and caesium (Schreuer, 1999*b*) have been reported recently. However, no structural characterizations of cyclic sulfamates have yet appeared in the literature, and the structural investigation of the title compound, (I), is part of our continuing research on the synthesis of artificial sweeteners and their metal complexes.

The Na^+ cation is seven-coordinated by three O atoms of sulfamate sulfonyl groups, two O atoms of two sulfamate nitro groups and the O atoms of two water molecules (Fig. 1). The geometry around the Na^+ centre is best described as a distorted monocapped trigonal prism with approximate C_{2v} symmetry. Each triangular face is defined by one O atom each from a water molecule, a nitro group and a sulfonyl group. The dihedral angle between the two triangular faces is 2.0°. An O atom from a sulfonyl group caps one of the square faces of the trigonal prism unsymmetrically. The structure consists of chains formed by the NaO_7 units. The O atoms of the water molecules and sulfonyl groups are bicoordinating and act as bridges between Na^+ centres. The nitro group also behaves as a bidentate donor between the cations.



(I)

The Na···Na separation is 3.6314 (6) Å. The Na—O distances involving water, sulfonyl and nitro O atoms are in the ranges 2.3247 (13)–2.4504 (14), 2.3843 (14)–2.8358 (15) and 2.4171 (14)–2.5985 (15) Å, respectively. All metal–oxygen distances are noticeably shorter in the title compound than in its potassium analogue (Bekdemir *et al.*, 2002). Although the K^+ ions exhibit two different coordination polyhedra, and involve coordination by sulfamate amine N atoms, all the Na^+ cations have the same geometry.

The phenyl and sulfamate rings are almost planar and lie in a plane with an r.m.s. deviation of 0.0361 Å (Fig. 2). The sulfamate ions adopt an antiparallel alignment between the chains and are connected to each other by weak C—H···O interactions [C2···O1(x, $1+y$, z) = 3.475 (2) Å] and π–π [$Cg\cdots Cg(-x, -y, 2-z)$ = 3.6931 (9) Å and $Cg\cdots Cg(\frac{1}{2}-x, \frac{1}{2}-y, 2-z)$ = 3.9450 (9) Å] interactions. The adjacent polyhedral chains are held together by strong hydrogen bonds. The water H atoms form O—H···N_{amine} hydrogen bonds (see Table 2) with the amine N atoms of neighboring sulfamate

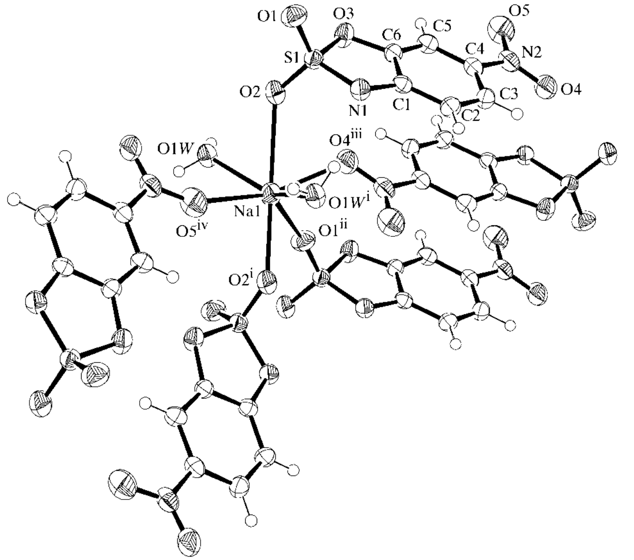


Figure 1
View of the title compound showing the coordination around the sodium ions. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, 2-z$; (iv) $x, -y, -\frac{1}{2}+z$.]

DOI: 10.1107/S0108270101017930

anions; the amine N atoms accept two hydrogen bonds. The hydrogen bonds, as well as the other intramolecular contacts, stabilize the crystal structure in the solid state, forming a three-dimensional network.

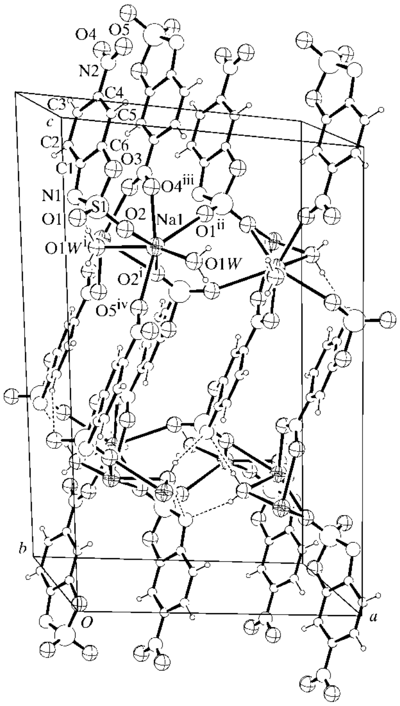


Figure 2
Part of the packing diagram of the title compound showing the hydrogen bonding. [Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, 2-z$; (iv) $x, -y, -\frac{1}{2}+z$.]

Experimental

6-Nitro-3-(*p*-tolylsulfonyl)-1,2,3-benzoxathiazole 2,2-dioxide (3.71 g, 10 mmol), alternatively named *N*-tosyl-*p*-nitrobenzoxasulfamate, prepared according to the method of Andersen & Kociolek (1995), was dissolved in acetonitrile (200 ml). NaN_3 (0.65 g, 10 mmol) was dissolved in water (*ca* 2 ml) and added dropwise to the first solution. The mixture was stirred by means of a magnetic stirrer at room temperature for 1 h. The solvent was removed under reduced pressure and the title compound was collected as a yellow solid. The solid was washed with chloroform and recrystallized from a tetrahydrofuran–water (1/1) mixture.

Crystal data

$Na^+\cdot C_6H_3N_2O_5S^-\cdot H_2O$
$M_r = 256.17$
Monoclinic, $C2/c$
$a = 13.0610$ (7) Å
$b = 6.8155$ (4) Å
$c = 20.7293$ (11) Å
$\beta = 99.6770$ (10)°
$V = 1819.01$ (17) Å^3
$Z = 8$
$D_x = 1.871$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3359 reflections
$\theta = 3.2$–27.5°
$\mu = 0.42$ mm^{-1}
$T = 298$ (2) K
Column, yellow
0.55 × 0.16 × 0.11 mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\min} = 0.761$, $T_{\max} = 0.949$
6528 measured reflections
2096 independent reflections
1758 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\max} = 27.5°$
$h = -16 \rightarrow 15$
$k = -8 \rightarrow 7$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.085$
$S = 1.04$
2096 reflections
151 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.050P)^2 + 0.652P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.37$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

S1—O1	1.4257 (13)	Na1—O1^{ii}	2.8355 (15)
S1—O2	1.4312 (12)	Na1—O2^{i}	2.3846 (14)
S1—O3	1.6442 (11)	Na1—O2	2.7644 (15)
S1—N1	1.5889 (13)	Na1—O4^{iii}	2.4173 (14)
Na1—O1W	2.3244 (14)	Na1—O5^{iv}	2.5988 (15)
Na1—O1W^{i}	2.4516 (15)	Na1—Na1^{v}	3.6314 (6)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1W1$\cdots$N1^{i}	0.811 (9)	2.173 (12)	2.9521 (17)	161 (2)
O1W—H2W1$\cdots$N1^{ii}	0.821 (9)	2.196 (12)	2.9859 (17)	161 (2)
C2—H2$\cdots$O1^{iii}	0.93	2.57	3.475 (2)	166

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

Water H atoms were found in difference maps and were positionally refined with geometric restraints (O—H = 0.82 and H$\cdots$H = 1.30 Å) and with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) (Sheldrick, 1997). Other H atoms were placed in calculated positions (C—H = 0.93 Å), with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997).

The authors thank Ondokuz Mayıs University for the financial support given to the project.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1465). Services for accessing these data are described at the back of the journal.

References

Andersen, K. K. & Kociolek, M. G. (1995). *J. Org. Chem.* **60**, 2003–2007.
Bekdemir, Y., Kutuk, H., Celik, S., Yilmaz V. T. & Thoene, C. (2002). *J. Mol. Struct.* **604**, 239–244.
Bruker (1999). *SADABS*, *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Drew, M. G. B., Wilden, G. R. H., Spillane, W. J., Walsh, M. R., Ryder C. A. & Simmie, J. M. J. (1998). *Agr. Food Chem.* **46**, 3016–3026.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Schreuer, J. (1999*a*). *Z. Kristallogr.* **214**, 305.
Schreuer, J. (1999*b*). *Z. Kristallogr.* **214**, 306.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spillane, W. J., Ryder, C. A., Walsh, M. R., Curran, P. J., Concagh, D. G. & Wall, S. N. (1996). *Food Chem.* **56**, 255–261.
Stade, J., Held, P. & Bohaty, L. (2001). *Cryst. Res. Technol.* **36**, 347–360.