Structure of 6-Nitro-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxide Sodium Salt (6-Nitrosaccharin) at 123 K based on Neutron Diffraction Data

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Abstract. $Na^+.C_7H_3N_2O_5S^-.4H_2O$, $M_r = 322.1$, triclinic, $P\bar{1}$, $a = 12.807$ (5), $b = 7.258$ (3), $c = 7.612$ (4) Å, $\alpha = 72.71$ (4), $\beta = 74.31$ (4), $\gamma = 75.34$ (3)°, $V = 638.8$ Å^3, $Z = 2$, $D_N = 1.657$ g cm^{-3}, $\lambda_N = 1.1756$ Å, $\mu = 1.545$ cm^{-1}, $F(000) = 332$, $T = 123$ K, final $R(F^2) = 0.065$, $wR(F^2) = 0.068$ for 1894 independent observed reflections. Two of the four water molecules are disordered. The molecule is planar. The bond lengths and angles conform with those of similar compounds. The Na^+ ion has sixfold coordination with six O atoms in a distorted octahedron.

Introduction. As a continuation of our program to investigate charge-density distributions of saccharin derivatives with different taste properties, we have undertaken a neutron structure analysis of the title compound to provide parameters for $X - N$ difference electron density maps. The title compound is a saccharin derivative with a bitter taste. In this work its structure is compared with the structure of UH-AF 50 NA (Rudert, Buschmann, Luger, Gregson & Trummlitz, 1988), a sweet-tasting saccharin derivative.

Experimental. The preparation of 6-nitrosaccharin is described by Rose (1969). The sodium salt is obtained by addition of the calculated amount of sodium hydroxide in ethanol, subsequent evaporation to dryness and recrystallization from 2-propanol/water (m.p. above 620 K). Crystals suitable for neutron structure analysis were grown from water. The crystals were extremely unstable in dry air, so they had to be placed in quartz capillaries. Two crystals had to be used for the measurement, one of approximate size $2.8 \times 5.5 \times 1.5$ mm, the other $2.2 \times 4.4 \times 1.1$ mm, the shapes being prismatic. Diffractometer used: four-circle instrument P32 at the CENG Siloe Reactor, Grenoble. Cryostat: single-stage closed-cycle refrigerator CS

1003 (Allibon, Filhol, Lehmann, Mason & Simms, 1981). The temperature controller was calibrated using a crystal of KH_2PO_4 which has a phase transition at 123 K (Schenk & Weckermann, 1969). Cell dimensions from 17 reflections in the range $18° < \theta < 34°$. Absorption corrections: program *ABSORB* of *XTAL* (Gaussian integration) (Stewart & Hall, 1986); min., max. transmission factors 0.792, 0.871 (first crystal) and 0.850, 0.909 (second crystal). Intensity measurements: $\omega/2\theta$ step scan, $(\sin\theta)/\lambda < 0.5921$ Å^{-1}, $-15 < h < 15$, $-9 < k < 9$, $-9 < l < 8$. 2 standard reflections, no intensity variation. 2878 reflections recorded, 1894 independent observed, 634 independent unobserved $[I < 2\sigma(I)]$. Initial coordinates for the compound taken from X-ray analysis (Luger, 1986). Least-squares refinement: function minimized $\sum w(F_o{}^2 - F_c{}^2)^2$, $w = 1/\sigma^2(F_o{}^2)$. Computer program: *XTAL* (Stewart & Hall, 1986). Refinement was made with 296 variables including anisotropic temperature factors except for the disordered H atoms, including an isotropic extinction parameter, model of Larson (1969), lowest F_c correcting factor 0.90. The ratio of maximum least-squares shift to e.s.d. in final refinement cycle: 0.22. Final $S(F^2) = 2.68$. Neutron scattering length for N taken from Koester & Yellon (1982), all others from Koester & Rauch (1982).

Discussion. The final atomic coordinates and the temperature factors are given in Table 1.* Fig. 1 is an *ORTEP* plot of the molecule and Fig. 2 is a projection

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* Lists of anisotropic thermal parameters, observed and calculated neutron structure amplitudes, all bond lengths and angles and dihedral angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51712 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of the unit cell. The atom-numbering scheme is the same as in UH-AF 50 NA. Two of the four water molecules (Nos. 3 and 4) are disordered. This disorder has been resolved completely with population parameters of 0·5 for the two counterparts. The disorder has not been found in a room-temperature X-ray measurement of the same compound (Luger, 1986). The title compound differs from UH-AF 50 NA by the absence of the OH group at C(5) and the additional NO$_2$ group at C(7). The molecule is planar: the maximum distance from the least-squares plane of the five- and six-membered rings including N(7) and O(3) is 0·066 (4) Å. The distance of Na$^+$ from the plane is 0·554 (6) Å. Table 2 shows the bond distances of the five-membered ring in comparison with those of UH-AF 50 NA. Within the standard deviations no difference can be seen. There is also no significant

difference between the bond lengths in the six-membered ring of the title compound and of UH-AF 50 NA. Only the C(5)—C(6) bond is somewhat shorter in

Table 1. *Neutron atomic coordinates and equivalent isotropic temperature factors* (Å^2 × 10^2) *for 6-nitrosaccharin at 123 K*

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

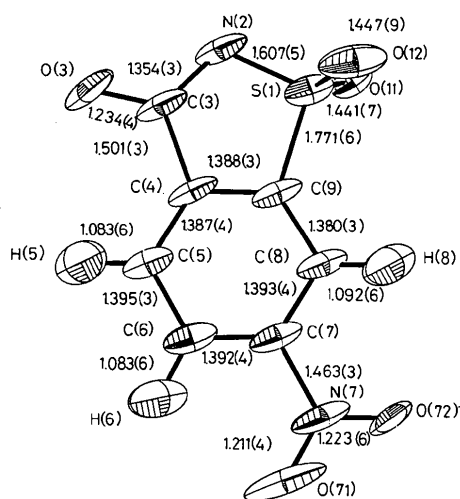|	x	y	z	U_{eq}
Na	0·4946 (3)	0·2587 (6)	0·4851 (8)	3·2 (1)
S(1)	−0·1375 (4)	0·8762 (9)	0·6793 (9)	3·1 (2)
O(11)	−0·1578 (2)	0·9392 (4)	0·4913 (4)	2·97 (8)
O(12)	−0·1020 (2)	1·0176 (5)	0·7392 (6)	5·1 (1)
N(2)	−0·2417 (1)	0·7979 (3)	0·8293 (3)	3·53 (6)
C(3)	−0·2160 (2)	0·6049 (5)	0·9143 (4)	3·58 (9)
O(3)	−0·2813 (2)	0·5098 (7)	1·0356 (5)	5·3 (1)
C(4)	−0·0983 (2)	0·5142 (4)	0·8465 (4)	3·02 (8)
C(5)	−0·0436 (2)	0·3243 (4)	0·9100 (4)	3·12 (9)
C(6)	0·0682 (2)	0·2743 (4)	0·8305 (4)	3·44 (9)
C(7)	0·1204 (2)	0·4146 (4)	0·6903 (4)	3·45 (8)
N(7)	0·2373 (1)	0·3591 (3)	0·6063 (4)	4·56 (8)
O(71)	0·2921 (2)	0·2181 (7)	0·6937 (6)	6·6 (1)
O(72)	0·2743 (3)	0·4570 (5)	0·451 (1)	8·9 (2)
C(8)	0·0672 (2)	0·6057 (4)	0·6224 (5)	3·65 (9)
C(9)	−0·0425 (2)	0·6503 (4)	0·7084 (4)	3·11 (8)
O(1W)	0·4926 (3)	0·4096 (4)	0·7294 (5)	2·9 (1)
O(2W)	0·4568 (3)	0·0715 (4)	0·3072 (5)	3·4 (1)
O(3W1)	0·6152 (7)	0·102 (1)	−0·001 (1)	1·7 (2)
O(4W1)	0·6854 (4)	0·2399 (9)	0·395 (1)	2·7 (2)
O(3W2)	0·6298 (7)	0·177 (1)	−0·040 (1)	1·8 (3)
O(4W2)	0·6795 (4)	0·1996 (7)	0·2770 (9)	2·2 (2)
H(11W)	0·4245 (5)	0·4161 (8)	0·8197 (9)	4·7 (2)
H(21W)	0·5472 (4)	0·3280 (8)	0·8008 (9)	4·7 (2)
H(12W)	0·5113 (5)	0·083 (1)	0·193 (1)	6·7 (3)
H(22W)	0·3864 (5)	0·1132 (9)	0·271 (1)	5·9 (2)
H(13W1)	0·6541 (8)	0·128 (2)	0·074 (2)	3·9 (2)
H(23W1)	0·6568 (9)	−0·011 (2)	−0·044 (2)	3·6 (2)
H(14W1)	0·7359 (9)	0·127 (2)	0·425 (2)	3·5 (2)
H(24W1)	0·7100 (9)	0·306 (2)	0·266 (3)	3·3 (3)
H(13W2)	0·6717 (8)	0·261 (2)	−0·025 (1)	3·7 (2)
H(23W2)	0·681 (1)	0·058 (2)	−0·067 (2)	3·2 (2)
H(14W2)	0·7323 (8)	0·110 (2)	0·347 (2)	3·3 (2)
H(24W2)	0·7111 (8)	0·310 (2)	0·199 (2)	3·0 (3)
H(5)	−0·0857 (4)	0·2172 (9)	1·019 (1)	4·9 (2)
H(6)	0·1154 (4)	0·1288 (9)	0·876 (1)	5·1 (2)
H(8)	0·1095 (4)	0·7124 (9)	0·510 (1)	5·2 (2)

Fig. 1. *ORTEP* plot (Johnson, 1976) of the title compound. Ellipsoids are at the 67% probability level. Bond lengths in Å, e.s.d.'s in parentheses.

Table 2. *Bond distances of the five-membered ring of 6-nitrosaccharin and UH-AF 50 NA in* Å

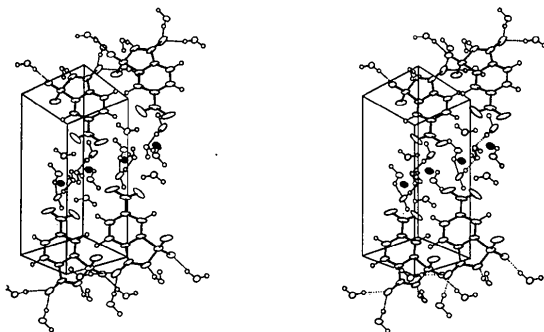|	6-Nitrosaccharin	UH-AF 50 NA
S(1)—N(2)	1·607 (5)	1·604 (8)
S(1)—C(9)	1·771 (6)	1·759 (8)
S(1)—O(11)	1·441 (7)	1·442 (5)
N(2)—C(3)	1·354 (3)	1·358 (4)
C(3)—O(3)	1·234 (4)	1·238 (5)
C(3)—C(4)	1·501 (3)	1·505 (4)
C(4)—C(9)	1·388 (3)	1·386 (5)

Fig. 2. Projection of the unit cell. Hydrogen bonds are drawn as dotted lines. The Na$^+$ cations are black circles.

Table 3. *Neutron bond angles of 6-nitrosaccharin in* °

O(11)—S(1)—O(12)	115·5 (4)	O(11)—S(1)—N(2)	111·1 (4)
O(11)—S(1)—C(9)	110·5 (4)	O(12)—S(1)—N(2)	111·0 (4)
O(12)—S(1)—C(9)	110·0 (4)	N(2)—S(1)—C(9)	97·3 (3)
S(1)—N(2)—C(3)	111·7 (2)	N(2)—C(3)—O(3)	124·5 (3)
N(2)—C(3)—C(4)	113·2 (2)	O(3)—C(3)—C(4)	122·3 (3)
C(3)—C(4)—C(5)	128·2 (2)	C(3)—C(4)—C(9)	111·2 (2)
C(5)—C(4)—C(9)	120·5 (2)	C(4)—C(5)—C(6)	118·2 (2)
C(4)—C(5)—H(5)	121·3 (3)	C(6)—C(5)—H(5)	120·5 (4)
C(5)—C(6)—C(7)	119·3 (2)	C(5)—C(6)—H(6)	121·5 (4)
C(7)—C(6)—H(6)	119·2 (3)	C(6)—C(7)—N(7)	118·7 (2)
C(6)—C(7)—C(8)	123·6 (2)	N(7)—C(7)—C(8)	117·7 (2)
C(7)—N(7)—O(71)	118·4 (2)	C(7)—N(7)—O(72)	118·2 (2)
O(71)—N(7)—O(72)	123·4 (2)	C(7)—C(8)—C(9)	115·1 (2)
C(7)—C(8)—H(8)	122·3 (3)	C(9)—C(8)—H(8)	122·6 (3)
S(1)—C(9)—C(4)	106·6 (2)	S(1)—C(9)—C(8)	130·2 (3)
C(4)—C(9)—C(8)	123·1 (2)		

Table 4. *Coordination distances of the sodium cation in Å*

Na⁺···X		Symmetry operation for X
Na⁺···O(1W)	2·415 (7)	x, y, z
Na⁺···O(1W)	2·491 (5)	1−x, 1−y, 1−z
Na⁺···O(2W)	2·386 (7)	x, y, z
Na⁺···O(2W)	2·482 (5)	1−x, −y, 1−z
Na⁺···O(4W1)	2·332 (6)	x, y, z
Na⁺···O(4W2)	2·482 (6)	x, y, z
Na⁺···O(71)	2·685 (5)	x, y, z

Table 5. *Hydrogen bridges, distances in Å*

X−H···Y	X···Y	X−H	H···Y	Symmetry operation for Y
O(1W)−H(11W)···O(3)	2·840 (4)	0·952 (6)	1·906 (6)	−x, 1−y, 2−z
O(1W)−H(21W)···O(3W1)	2·983 (9)	0·969 (7)	2·06 (1)	x, y, 1+z
O(2W)−H(12W)···O(3W1)	3·36 (1)	0·953 (8)	1·70 (1)	x, y, z
O(2W)−H(22W)···N(2)	3·034 (4)	0·962 (8)	2·074 (7)	−x, 1−y, 1−z
O(3W1)−H(23W1)···N(2)	2·87 (1)	0·95 (2)	1·94 (1)	1+x, −1+y, −1+z
O(4W1)−H(14W1)···O(11)	2·638 (6)	0·92 (1)	1·73 (1)	1+x, −1+y, z
O(4W1)−H(24W1)···O(3)	2·851 (7)	0·96 (2)	1·93 (2)	1+x, y, −1+z
O(1W)−H(21W)···O(3W2)	2·72 (1)	0·97 (7)	1·76 (1)	x, y, 1+z
O(2W)−H(12W)···O(3W2)	2·998 (9)	0·953 (8)	2·07 (1)	x, y, 1+z
O(3W2)−H(23W2)···N(2)	3·12 (1)	0·98 (1)	2·17 (1)	1+x, −1+y, −1+z
O(4W2)−H(14W2)···O(11)	2·93 (6)	0·96 (1)	1·97 (1)	1+x, −1+y, z
O(4W2)−H(24W2)···O(3)	2·512 (6)	0·95 (1)	1·62 (1)	1+x, y, −1+z

the title compound [1·395 (3) Å] than in UH-AF 50 NA [1·411 (5) Å]. The bond angles are given in Table 3. The Na⁺ ion is sixfold coordinated. The coordination polyhedron is a distorted octahedron, consisting of five O atoms from the water molecules and one from the NO₂ group. The coordination distances can be seen in Table 4. There are seven intermolecular hydrogen bridges, two between water molecules, the others between one water molecule and the 6-nitrosaccharin molecule (Table 5). The disordered water molecules are involved in five of the hydrogen bridges.

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Structure of Bis[μ-N,N'-(o-phenylene)thiourea-S]-bis[N,N'-(o-phenylene)thiourea-S]-selenium(II)} Perchlorate Hexahydrate

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Abstract. [Se₂(C₇H₆N₂S)₆](ClO₄)₄.6H₂O, M_r = 1564, monoclinic, $P2_1$, a = 17·089 (3), b = 10·741 (2), c = 17·506 (4) Å, β = 108·2 (1)°, V = 3053·0 Å³, Z = 2, D_x = 1·70 g cm⁻³, λ(Cu Kα) = 1·5418 Å, μ = 54·79 cm⁻¹, F(000) = 1584, T = 283 K, final R = 0·069 for 3980 observed reflections. A dinuclear complex formation with planar SeS₄ groups sharing two

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* N,N'-(o-Phenylene)thiourea is 2(3H)-benzimidazolethione.
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