only small discrepancies. Several starting conformations for (5*a*) and (5*b*) were explored and from each a six-step approach to the target was forced. Considering only the lowest-energy paths, we found that the increase in energy of (5*b*) as it approached the (6*b*) target conformation was 6·3 to 8·4 kJ less than the energy increase of (5*a*) as it approached the (6*a*) conformation. This is a quantitation of the idea that the more bulky dimethylamino groups, which are also closer to the P atom, make it more difficult for the azide N atom to approach the P atom than when the substituents are phenyl groups.

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Structure of 4-Hydroxy-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxide Sodium Salt (UH-AF 50 NA) at 123 K based on Neutron Diffraction Data

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Abstract. $Na^+.C_7H_4NO_4S^-.H_2O$, $M_r = 239·2$, orthorhombic, *Pnam*, $a = 10·842\ (6)$, $b = 12·042\ (6)$, $c = 6·910\ (1)$ Å, $V = 902·2$ Å^3, $Z = 4$, $D_N = 1·760$ g cm^{-3}, $\lambda_N = 1·1756$ Å, $\mu = 1·194$ cm^{-1}, $F(000) = 488$, $T = 123$ K, final $R(F^2) = 0·079$, $wR(F^2) = 0·110$ for 937 independent observed reflections. The molecule lies on the mirror plane except for the SO_2 O atoms and the water H atoms. The Na^+ cation has sixfold coordination with one N and five O atoms in a distorted octahedron.

Introduction. As part of a program to investigate charge-density distributions of saccharin derivatives, a neutron structure analysis of the title compound, UH-AF 50 NA, was performed to provide accurate atomic parameters for a three-dimensional difference Fourier synthesis of an *X*–*N* deformation electron density distribution that could not be obtained by X-ray diffraction on account of low scattering power at high angles. UH-AF 50 NA is a new non-nutritive sweetener and will be compared with other saccharin derivatives

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that have bitter taste properties. When comparing structurally similar compounds with different taste properties, the object is to obtain experimental results that allow a correlation between taste and structure and/or electron distribution. Quantum chemical calculations of the charge distribution in different saccharin derivatives performed by Trummlitz (1986) show that small differences in the electron-density distribution of the relevant molecular regions can be expected.

Experimental. Crystals suitable for neutron structure analysis were grown from water. Diffractometer used: four-circle instrument *P*32 at the CENG Siloe Reactor, Grenoble, France. 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 20 reflections in the range $15° < \theta < 35°$; prismatic crystals, approximate crystal dimensions $3{\cdot}5 \times 1{\cdot}65 \times 1{\cdot}3$ mm, volume 6·31 mm^3. Absorption corrections: program *ABSORB* with Gaussian integration of the *XTAL* system (Stewart & Hall, 1986); max. and min. transmission factors 0·862 and 0·811. Intensity measurements: $\omega/2\theta$ step scan, $(\sin\theta)/\lambda < 0{\cdot}651$ Å^{-1}, $0 \le h \le 14$, $0 \le k \le 15$, $0 \le l \le 8$. 1360 reflections recorded, 937 independent observed, 215 unobserved $[I < 2\sigma(I)]$. Repeated measurement of a standard reflection showed significant intensity variations caused by detector instabilities. Therefore the data set was subdivided into three scale groups. Initial coordinates for UH-AF 50 NA taken from X-ray analysis (Luger, 1984). Least-squares refinement, function minimized $\sum w(F_o^2 - F_c^2)^2$, $w = 1/\sigma^2(F_o^2)$, max. least-squares shift to e.s.d. in final refinement cycle 0·13. Computer programs from *XTAL* (Stewart & Hall, 1986). Refinement was made with 124 variables and included an isotropic extinction parameter, model of Larson (1969), lowest F_c correcting factor 0·77. Neutron scattering length for N taken from Koester & Yellon (1982), all others from Koester & Rauch (1982).

Table 1. *Neutron atomic coordinates and equivalent isotropic temperature factors* (Å^2 × 10^2) *for UH-AF* 50 *NA at* 123 K

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

	x	y	z	U_{eq}
Na(1)	0·9048 (6)	−0·3640 (5)	0·25000	1·0 (2)
S(1)	0·6604 (6)	0·0561 (7)	0·25000	0·6 (2)
O(1S)	0·6150 (2)	0·1089 (3)	0·0767 (5)	1·5 (1)
N(2)	0·6334 (2)	−0·0748 (2)	0·25000	1·1 (1)
C(3)	0·7396 (3)	−0·1346 (3)	0·25000	0·8 (1)
O(3)	0·7420 (3)	−0·2374 (3)	0·25000	1·2 (1)
C(4)	0·8531 (3)	−0·0627 (3)	0·25000	0·8 (1)
C(5)	0·9774 (3)	−0·0931 (3)	0·25000	0·9 (1)
O(5)	1·0099 (3)	−0·2006 (3)	0·25000	1·2 (1)
C(6)	1·0655 (3)	−0·0068 (3)	0·25000	1·2 (1)
C(7)	1·0309 (3)	0·1042 (3)	0·25000	1·6 (1)
C(8)	0·9066 (3)	0·1356 (3)	0·25000	1·3 (1)
C(9)	0·8224 (3)	0·0491 (3)	0·25000	0·9 (1)
O(1*W*)	0·3563 (4)	0·0661 (4)	0·25000	1·6 (1)
H(1*W*)	0·4004 (7)	0·0893 (5)	0·361 (1)	4·4 (2)
H(5)	1·1010 (6)	−0·2116 (6)	0·25000	2·2 (2)
H(6)	1·1629 (6)	−0·0296 (7)	0·25000	3·2 (3)
H(7)	1·1039 (7)	0·1653 (7)	0·25000	3·7 (3)
H(8)	0·8785 (8)	0·2214 (6)	0·25000	3·6 (3)

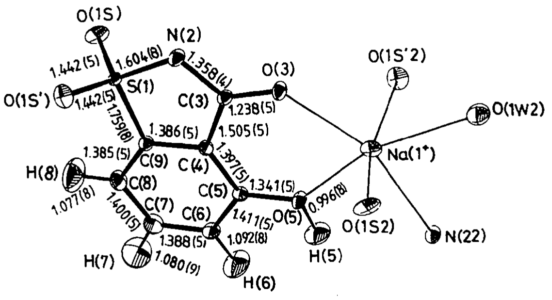

Fig. 1. The molecule of UH-AF 50 NA with the coordination octahedron. Ellipsoids are at the 67% probability level. Bond lengths in Å, e.s.d.'s in parentheses.

Discussion. The final atomic coordinates are given in Table 1.* An *ORTEP* view (Johnson, 1965) illustrates the molecular structure and the Na$^+$ coordination (Fig. 1). Because of its special position on the mirror plane the ring system is completely planar. Only the O atoms of the SO_2 group and the two H atoms of the water molecule lie outside this plane. Saccharin, of which the X-ray structure is known (Bart, 1968; Okaya, 1969), differs from UH-AF 50 NA in the absence of the OH group at C(5). The X-ray structures of Na, Mg (Jovanovski & Kamenar, 1982), Mn (Kamenar & Jovanovski, 1982), Hg (Kamenar, Jovanovski & Grdenić, 1982), Fe, Co, Ni, Cu (Haider, Malik, Ahmed, Hess, Riffel & Hursthouse, 1982), Zn, Cd (Haider, Malik, Das & Hursthouse, 1984) and K_2Na (Malik, Haider, Hossain & Hursthouse, 1984) saccharinates are also known.

Table 2 gives a comparison of a number of bond lengths and angles of related compounds. There is good agreement between the mean values of bond lengths and angles of the saccharinates and the neutron structure of UH-AF 50 NA. The other bond lengths and angles of the neutron structure are given in Fig. 1 and Table 3.

Because of the condensed five-membered ring there are characteristic deviations from an ideal benzene ring in the six-membered ring. The bond angle at C(9), for example, is greater than 120° while the angles at C(5) and C(8) are smaller than 120°. This has been found in all saccharinates and in saccharin itself. The C—OH

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* Lists of anisotropic thermal parameters and observed and calculated neutron structure amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44793 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Comparison of bond lengths and bond angles of* Na, Mg, Mn, Hg, Zn, Cd, K_2Na, Cu, Fe, Co *and* Ni *saccharinates with saccharin* (*Bart,* 1968) *and UH-AF* 50 *NA* (*this work*)

Bond lengths are in Å, angles in °.

	Saccharin (X-ray)	Mean value of Na, Mg, Mn, Hg, Zn, Cd, K_2Na, Cu, Fe, Co, Ni weighted with 1/e.s.d.	UH-AF 50 NA (neutron data)
S(1)–N(2)	1·663 (2)	1·628	1·604 (8)
S(1)–C(9)	1·761 (2)	1·755	1·759 (8)
S(1)–O(1)	1·427 (2)	1·442	1·442 (5)
N(2)–C(3)	1·375 (3)	1·358	1·358 (4)
C(3)–O(3)	1·220 (2)	1·238	1·238 (5)
C(3)–C(4)	1·480 (3)	1·498	1·505 (4)
C(4)–C(9)	1·385 (3)	1·383	1·386 (5)
C(9)–S(1)–N(2)	92·7 (1)	97·1	97·8 (4)
S(1)–N(2)–C(3)	115·0 (1)	110·9	111·5 (3)
N(2)–C(3)–C(4)	109·8 (2)	113·3	112·9 (3)
C(3)–C(4)–C(9)	112·6 (2)	111·2	111·2 (3)
C(4)–C(9)–S(1)	109·8 (1)	107·3	106·7 (4)

Table 3. *Neutron bond angles of UH-AF* 50 *NA in* ° (*angles of the five-membered ring: see Table* 2)

H(1*W*)–O(1*W*)–H(1*W*)	108·5 (8)	O(1S)–S(1)–N(2)	111·8 (4)
O(1S)–S(1)–C(9)	111·2 (3)	O(1S)–S(1)–O(1S)	112·3 (5)
N(2)–C(3)–O(3)	123·2 (3)	O(3)–C(3)–C(4)	124·0 (3)
C(3)–C(4)–C(5)	129·7 (3)	C(5)–C(4)–C(9)	119·1 (3)
C(4)–C(5)–O(5)	120·4 (3)	C(4)–C(5)–C(6)	117·4 (3)
O(5)–C(5)–C(6)	122·2 (3)	C(5)–O(5)–H(5)	112·9 (6)
C(5)–C(6)–C(7)	121·8 (3)	C(5)–C(6)–H(6)	118·0 (5)
C(7)–C(6)–H(6)	120·2 (5)	C(6)–C(7)–C(8)	121·3 (3)
C(6)–C(7)–H(7)	117·3 (5)	C(8)–C(7)–H(7)	121·4 (5)
C(7)–C(8)–C(9)	115·5 (3)	C(7)–C(8)–H(8)	122·1 (6)
C(9)–C(8)–H(8)	122·3 (6)	S(1)–C(9)–C(8)	128·5 (4)
C(4)–C(9)–C(8)	124·9 (3)	O(5)–H(5)–O(3)	165·7 (1)

bond C(5)–O(5) [1·341 (5) Å] is relatively short for a (phenyl)C–OH bond. In hydroquinone, for example, the bond length is 1·378 (3) Å (Lindeman, Shklover & Struchkov, 1981). But there exist literature examples which are comparable to our value, such as the bond length in 4-chloro-*N*-salicylideneaniline of 1·347 (3) Å (Lindeman, Shklover, Struchkov, Kravcheny & Potapov, 1982).

In the isothiazolone five-membered ring, the S–C bond has nearly the same value [1·759 (8) Å] as in saccharin [1·761 (2) Å]. The deprotonation at N(2) apparently results in a shortening of the S(1)–N(2) bond from 1·663 (2) Å (saccharin) down to 1·604 (8) Å (UH-AF 50 NA) and the N(2)–C(3) bond from 1·375 (3) Å down to 1·358 (4) Å. The inner angles of the five-membered ring of the saccharinates are also clearly different from those of the saccharin molecule.

The unit cell is displayed in Fig. 2. The molecules are situated on mirror planes at $z = \frac{1}{4}$ and $z = \frac{3}{4}$, so that the crystal structure is formed by layers having a distance of one half of a lattice constant in the z direction, *i.e.* 3·455 Å.

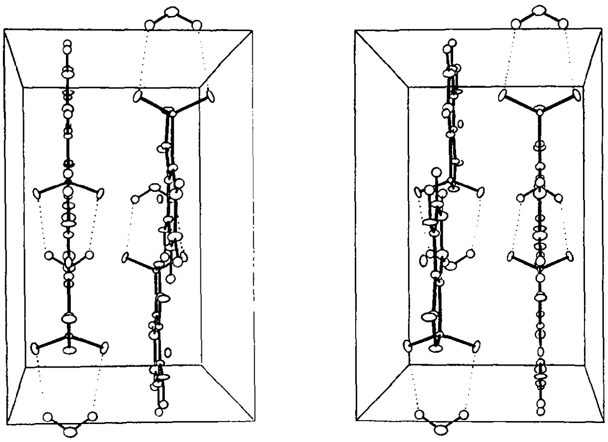

Fig. 2. Stereoview down the *b* axis, the *c* axis being horizontal. Hydrogen bonds are indicated by dotted lines.

Table 4. *Coordination distances* (Å) *of the* Na^+ *ion*

Na^+–O(3)	2·332 (7)	Na^+–N(2)	2·586 (7)
Na^+–O(5)	2·274 (8)	Na^+–O(1S)*	2·291 (4)
Na^+–O(1*W*)	2·490 (8)	Na^+–O(1S′)*	2·291 (4)

* O(1S) and O(1S′) are mirror-symmetric.

Table 5. *Hydrogen-bond distances* (Å) *in UH-AF* 50 *NA*

X–H···*Y*	*X*···*Y*	*X*–H	H···*Y*
O(1*W*)–H(1*W*)···O(1S)	3·093 (5)	0·948 (8)	2·378 (8)
O(5)–H(5)···O(3)	2·625 (5)	0·997 (8)	1·647 (8)

The Na^+ ion is sixfold coordinated, having five O and one N atoms in a distorted octahedron. For a given Na^+ cation the coordinated atoms are partly in the neighbouring layers, so that atoms of three different layers contribute to one coordination octahedron. The coordination distances are between 2·27 and 2·59 Å (see Table 4).

There are two intermolecular hydrogen bonds in the mirror plane: O(5)–H(5)···O(3) and O(1*W*)–H(1*W*)···O(1S) (see Table 5 and Fig. 2), and no hydrogen bonds between the layers.

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Two Polymorphs of 2-Bis[(2-hydroxyphenylmethylene)amino]methylphenol

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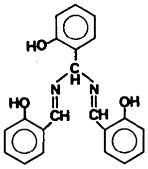
Abstract. $C_{21}H_{18}N_2O_3$, $M_r = 346{\cdot}4$, monoclinic, $C2/c$, $a = 17{\cdot}230\,(3)$, $b = 12{\cdot}322\,(2)$, $c = 19{\cdot}675\,(3)$ Å, $\beta = 121{\cdot}265\,(12)^\circ$, $V = 3571\,(2)$ Å^3, $Z = 8$, $D_x = 1{\cdot}289$ g cm^{-3}, $\lambda(\text{Cu}\,K\alpha) = 1{\cdot}54184$ Å, $\mu = 6{\cdot}70$ cm^{-1}, $F(000) = 1456$, $T = 296$ K, $R = 0{\cdot}039$ for 3209 observations (of 3691 unique data); triclinic, $P\bar{1}$, $a = 7{\cdot}678\,(2)$, $b = 10{\cdot}822\,(2)$, $c = 12{\cdot}539\,(2)$ Å, $\alpha = 63{\cdot}34\,(2)$; $\beta = 74{\cdot}92\,(2)$; $\gamma = 84{\cdot}04\,(2)^\circ$, $V = 899{\cdot}1\,(4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}279$ g cm^{-3}, $\lambda(\text{Cu}\,K\alpha) = 1{\cdot}54184$ Å, $\mu = 6{\cdot}65$ cm^{-1}, $F(000) = 364$, $T = 299$ K, $R = 0{\cdot}036$ for 3095 observations (of 3399 unique data). Distances and angles are quite similar in the two structures. There are two strong intramolecular hydrogen bonds between a phenolic oxygen and an imino nitrogen in each structure. The intermolecular hydrogen bonds between two phenolic oxygens are closer in the monoclinic crystal than in the triclinic. This closer packing produces the higher melting point for the monoclinic polymorph.

Introduction. In an effort to synthesize a functionalized imidazole, a reaction of salicylaldehyde with ammonia and glyoxal gave the title compound (I) instead of the desired product. Formation of the title compound was not surprising because aromatic aldehydes react readily with ammonia to give diimine derivatives. (Sandler & Karo, 1971). The title compound had been prepared several times in the past (Ettling, 1840; Herzfeld, 1877; Delepine & Rivals, 1899; Hantzsch, 1906; Liggett & Diehl, 1948; Kamal, Ahmad & Ali Qureshi, 1963; Kambe, Takajo & Satto, 1975) with reported melting points ranging from 431 to 440 K, except Herzfeld's 418 K. Our melting point, 416·5–417 K, agreed with the latter. We repeated the reaction without glyoxal and obtained the higher melting material, which appeared as a different crystalline form. A brief but unsuccessful effort was made to determine the conditions required for formation of one crystalline form over the other. Infrared, ^{1}H NMR, ^{13}C NMR and elemental analyses on the two materials agreed with those reported as well as with each other. These methods did not rule out the possibility of geometric isomers, prompting us to analyze both crystals by X-ray diffraction. Single-crystal X-ray analysis revealed that both imino bonds are *anti* in both crystals; thus we had prepared two polymorphs of the title compound.



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