the single order-parameter model, the Λ_2 distortion corresponds to a secondary mode (third harmonic of the primary mode Λ_3), whereas according to the other model, it plays the role of a primary mode. Taking into account the relative weights of the Λ_3 and Λ_2 modes from our analysis, we think that these results support the single soft-mode model, because otherwise a larger contribution from the Λ_2 mode could be expected. As a general conclusion to this work it can be said that the four-dimensional description and refinement of the modulated structure is comparable to the standard commensurate one. The former refinement, however, includes far fewer variables. On the other hand, we have found that the structure of the modulated fourfold phase of BCCD is essentially the same as that of the INC phase with a major contribution of the Λ_3 mode to the distortion. Accordingly, it can be expected that the structures of the different commensurate and INC phases appearing below 75 K are similar to that of the first INC phase except for the change of wavevector values and greater amplitude of the distortion.

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Structures of 4-Methoxy-, 5-Chloro-, 5-Nitro- and 6-Nitro-1,2-benzisothiazol-3(2*H*)-one 1,1-Dioxide Sodium Salt (4-Methoxy-, 5-Chloro-, 5-Nitro- and 6-Nitrosaccharin)

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Abstract

The crystal structures of four bitter-tasting saccharin derivatives have been solved. 4-Methoxysaccharin, $2Na^+.2C_8H_6NO_4S^-.3CH_3OH$, $M_r = 566.5$, monoclinic, $P2_1/c$, $a = 10.461$ (4), $b = 10.942$ (4), $c = 21.799$ (8) Å, $\beta = 96.97$ (3)°, $V = 2477$ (3) Å^3, $Z = 4$, $D_x = 1.519$ g cm^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, μ =

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Table 1. *Summary of intensity measurements and structure analyses*

	4-Methoxysaccharin	5-Chlorosaccharin	5-Nitrosaccharin	6-Nitrosaccharin
Intensity measurements				
Solvent for crystallization	Methanol	Water	Methanol	Water
Crystal size (mm)	0.25 × 0.25 × 1.5	0.62 × 0.20 × 0.15	0.45 × 0.35 × 0.09	0.5 × 0.2 × 0.2
Diffractometer	Stoe	Siemens AED	Siemens AED	Siemens AED
Radiation and filter	Cu $K\alpha$ (Ni)	Mo $K\alpha$ (Zr)	Mo $K\alpha$ (Zr)	Mo $K\alpha$ (Zr)
Min./max. $\sin\theta/\lambda$ (Å^{-1})	0.04/0.554	0.595/1.270	0.06/1.272	0.07/0.997
ω scan range (°)	1.66 + 0.25tanθ	0.86 + 0.25tanθ	1.58 + 0.25tanθ	1.38 + 0.25tanθ
No. of reflections measured	4146	6959	6401	11179
No. of unique reflections	4146	4897	5056	10652
No. of unobserved unique reflections	330	968	281	3153
Min. *hkl*	0 0 −24	0 0 −17	−37 −16 −11	−25 −14 −15
Max. *hkl*	11 12 24	11 67 17	38 16 0	24 13 0
No. of standard reflections	2	6	7	2
max. deviation (%)	8.3	2.6	1.0	1.0
Structure analyses				
Min./max. absorption correction factor	No correction	1.10/1.19	1.03/1.14	1.08/1.11
No. of variables	373	159	173	244
$wR(F^2)$*	–	0.088†	0.084†	0.101
$R(F^2)$	0.074 [$R(F)$]	0.080†	0.072†	0.089
$R_w(F) = \Sigma(\Delta F/F)$	–	0.045	0.013	0.076
S	–	1.30†	1.19†	2.73

* $w = 1/\sigma^2(F^2)$.
† High-order refinement, $\sin\theta/\lambda > 0.60$ Å^{-1}.

2.78 mm^{-1}, $F(000) = 1176$, room temperature, final $R(F) = 0.074$ for 3816 unique observed reflections. 5-Chlorosaccharin, $Na^+.C_7H_3ClNO_3S^-.H_2O$, M_r = 257.6, monoclinic, $P2_1/n$, $a = 4.710$ (1), b = 29.686 (7), $c = 6.982$ (2) Å, $\beta = 92.19$ (2)°, V = 975.5 (7) Å^3, $Z = 4$, $D_x = 1.754$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.64$ mm^{-1}, $F(000) = 520$, T = 128 K, final $R(F^2) = 0.080$ for 3929 unique observed reflections. 5-Nitrosaccharin, $Na^+.C_7H_3N_2O_5S^-.H_2O$, $M_r = 268.2$, monoclinic, $P2_1$, $a = 15.559$ (4), b = 6.788 (4), $c = 4.753$ (2) Å, $\beta = 92.31$ (2)°, V = 501.6 (4) Å^3, $Z = 2$, $D_x = 1.776$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.39$ mm^{-1}, $F(000) = 272$, T = 123 K, final $R(F^2) = 0.066$ (full-order refinement) for 4775 unique observed reflections. 6-Nitrosaccharin, $Na^+.C_7H_3N_2O_5S^-.4H_2O$, $M_r = 322.2$, triclinic, $P\bar{1}$, a = 12.827 (5), $b = 7.276$ (3), $c = 7.616$ (4) Å, α = 72.69 (4), $\beta = 74.33$ (4), $\gamma = 75.29$ (3)°, V = 641.6 (9) Å^3, $Z = 2$, $D_x = 1.668$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.34$ mm^{-1}, $F(000) = 332$, T = 123 K, final $R(F^2) = 0.089$ for 7499 unique observed reflections. The structures of 5-chloro- and 5-nitrosaccharin are very similar and differ from those of the other compounds. In each of the four structures the Na cations are coordinated sixfold and form distorted coordination octahedra. A presumed correlation between the C—O bond length in the isothiazolone ring and taste is discussed.

Introduction

This study is part of a series of structure and electron density investigations of sweet- and bitter-tasting saccharin derivatives (Rudert, Buschmann, Luger, Gregson & Trummlitz, 1988, 1989; Rudert, Buschmann, Richter, Luger & Trummlitz, 1991). The aim of the series is to find a correlation between structure and electron density on the one hand, and taste on the other. CNDO/2 calculations (CNDO = complete neglect of differential overlap) predicting differences in the charge distributions in the N—C—O part of the isothiazolone ring stimulated these investigations. In this work the X-ray structures of four bitter saccharin derivatives, of which only 5-chlorosaccharin has a sweet by-taste, are presented.

Experimental

The crystals of 6-nitrosaccharin and especially those of 4-methoxysaccharin were very unstable in the air. All crystals used for X-ray measurements were therefore enclosed in glass capillaries. 4-Methoxysaccharin, additionally, had to be prepared together with its mother liquor. For this reason low-temperature data collection was not attempted. The other three determinations took place at temperatures between 123 and 128 K. On the four-circle diffractometer the crystals were cooled by a cold nitrogen gas stream of which the outer part was heated to prevent icing. The temperature was stable within ± 2 K. The intensity measurements were performed in the $\omega/2\theta$ step scan mode. For further details see Table 1.

For 5-chlorosaccharin, 6959 reflections were collected of which 805 were rejected because of suspected overlap with neighbouring reflections [large cell edge $b = 29.686$ (7) Å]. Of the remaining reflections 4897 were independent and of these 3929 were treated as 'observed' [$F_o > 2\sigma(F_o)$]. No data below $\sin\theta/\lambda = 0.595$ Å^{-1} were measured. In the high-order part of the data of 5-chloro- and 5-nitrosaccharin, only the intensities of the strongest reflections were measured ($\sin\theta/\lambda > 0.81$ and $\sin\theta/\lambda > 0.97$ Å^{-1}, respectively). The strong reflections were taken from lists of F_c values calculated from the structure of the

lower-order data. An absorption correction was applied to the three low-temperature data sets.

Structure determination

The structures of 5-chloro- and 6-nitrosaccharin were already known from previous room-temperature measurements [not published; solved by *MULTAN* (Main, Woolfson & Germain, 1975)]. The structure of 4-methoxysaccharin was determined by *MULTAN* and the structure of 5-nitrosaccharin by the program *MITHRIL* (Gilmore, 1983).

Refinement

The refinement program used was *XTAL* (Stewart & Hall, 1986). Refinements of 4-methoxy- and 6-nitrosaccharin were performed using all reflections, minimizing $R(F)$ for 4-methoxy- and $wR(F^2)$ for 6-nitrosaccharin. For the other two structures only high-order data ($\sin\theta/\lambda > 0.60$ Å^{-1}) were used, minimizing $wR(F^2)$. An additional full-order refinement was made for 5-nitrosaccharin to check the quality of the measurement. The unusually long crystal of 4-methoxysaccharin (Table 1) may be responsible for the poor R value, $R(F) = 0.074$.

Atomic scattering factors and anomalous-dispersion corrections for Na and S atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The positions of the methanol H atoms in 4-methoxysaccharin were calculated and kept fixed during further refinement. The isotropic displacement parameters of these H atoms were constrained to those of their bonding partners. For 5-chloro- and 5-nitrosaccharin isotropic displacement parameters were refined for the H atoms and anisotropic ones for the other atoms.

In 6-nitrosaccharin two of the four water molecules are disordered [molecules (3) and (4), atom labels 3*W* and 4*W*]. Two pairs of population parameters, each equal to 0.5, were used. The positions of the H atoms of water molecule 4 were kept fixed to the values of the neutron measurement. One isotropic extinction parameter (model by Zachariasen, 1967) was refined, $g = 1.6 \times 10^4$.

Results and discussion

The final atomic parameters and interatomic distances and angles are given in Tables 2, 3, 4 and 5.*

* Lists of H-atom parameters, anisotropic thermal parameters, observed and calculated X-ray structure amplitudes, all bond lengths and angles, dihedral angles, hydrogen bonds, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54827 (170 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BX0565]

Table 2. *Atomic parameters of non-*H *atoms and equivalent isotropic displacement parameters* (Å$^2 \times 10^2$)

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

	x	y	z	U_{eq}
4-Methoxysaccharin				
O(1*M*)	−0.2569 (3)	0.5102 (2)	0.3878 (1)	5.82 (8)
C(1*M*)	−0.2497 (5)	0.5396 (4)	0.3249 (2)	7.5 (2)
O(2*M*)	−0.3043 (3)	0.3105 (2)	0.4850 (1)	5.46 (8)
C(2*M*)	−0.3344 (5)	0.1838 (4)	0.4892 (3)	7.7 (2)
O(3*M*)	0.3989 (5)	0.0268 (5)	0.6309 (3)	12.3 (2)
C(3*M*)	0.4691 (7)	0.1328 (6)	0.6434 (4)	11.4 (3)
Na$^+$(1)	−0.1006 (1)	0.3928 (1)	0.46161 (6)	5.56 (5)
Na$^+$(2)	0.5456 (1)	0.4541 (1)	0.43084 (6)	5.10 (4)
S(11)	0.29811 (8)	0.59615 (8)	0.33406 (4)	5.18 (3)
O(11)	0.2761 (3)	0.7087 (3)	0.3001 (1)	6.54 (9)
O(12)	0.4308 (3)	0.5581 (3)	0.3445 (1)	6.43 (9)
N(12)	0.2363 (3)	0.5976 (3)	0.3982 (1)	5.8 (1)
C(13)	0.1427 (3)	0.5129 (3)	0.3987 (2)	5.0 (1)
O(13)	0.0826 (3)	0.4975 (2)	0.4432 (1)	5.79 (8)
C(14)	0.1192 (3)	0.4408 (3)	0.3397 (2)	4.7 (1)
C(15)	0.0314 (3)	0.3473 (3)	0.3224 (2)	5.0 (1)
O(15)	−0.0435 (3)	0.3069 (2)	0.3649 (1)	5.81 (8)
C(151)	−0.1268 (6)	0.2052 (5)	0.3486 (3)	7.3 (2)
C(16)	0.0248 (4)	0.3008 (4)	0.2623 (2)	5.9 (1)
C(17)	0.1055 (5)	0.3441 (4)	0.2218 (2)	6.5 (1)
C(18)	0.1973 (4)	0.4324 (4)	0.2386 (2)	5.9 (1)
C(19)	0.1996 (3)	0.4790 (3)	0.2977 (2)	5.1 (1)
S(21)	0.13585 (9)	0.17988 (8)	0.52057 (4)	5.28 (3)
O(21)	0.1577 (3)	0.0841 (3)	0.5663 (1)	6.7 (1)
O(22)	0.0040 (3)	0.2218 (3)	0.5100 (1)	6.7 (1)
N(22)	0.2347 (3)	0.2903 (3)	0.5355 (1)	5.6 (1)
C(23)	0.3114 (3)	0.3073 (3)	0.4903 (2)	4.7 (1)
O(23)	0.3931 (2)	0.3886 (2)	0.4925 (1)	5.31 (8)
C(24)	0.2864 (3)	0.2150 (3)	0.4393 (2)	4.6 (1)
C(25)	0.3432 (3)	0.1992 (3)	0.3852 (2)	5.0 (1)
O(25)	0.4385 (3)	0.2780 (2)	0.3741 (1)	5.67 (8)
C(251)	0.4954 (6)	0.2600 (5)	0.3179 (2)	7.3 (2)
C(26)	0.3007 (4)	0.1038 (4)	0.3459 (2)	6.2 (1)
C(27)	0.2040 (4)	0.0249 (4)	0.3595 (2)	6.8 (1)
C(28)	0.1450 (4)	0.0399 (4)	0.4120 (2)	6.2 (1)
C(29)	0.1889 (3)	0.1350 (3)	0.4504 (2)	5.0 (1)
5-Chlorosaccharin				
O(1*W*)	0.6784 (3)	0.45315 (4)	0.2602 (2)	1.64 (2)
Na$^+$(1)	½	½	½	1.36 (2)
Na$^+$(2)	½	½	1	1.37 (2)
S(1)	1.00336 (7)	0.43714 (1)	0.73514 (4)	1.095 (6)
O(11)	1.1632 (2)	0.44057 (4)	0.5617 (1)	1.56 (2)
O(12)	0.7916 (2)	0.47263 (4)	0.7513 (1)	1.42 (2)
N(2)	1.2055 (2)	0.43442 (4)	0.9234 (1)	1.36 (2)
C(3)	1.1690 (3)	0.39503 (4)	1.0198 (2)	1.33 (2)
O(3)	1.3013 (3)	0.38461 (5)	1.1708 (2)	1.96 (2)
C(4)	0.9497 (3)	0.36488 (5)	0.9245 (2)	1.33 (2)
C(5)	0.8486 (3)	0.32379 (5)	0.9893 (2)	1.64 (3)
C(6)	0.6375 (3)	0.30293 (5)	0.8744 (2)	1.71 (3)
Cl(6)	0.4889 (1)	0.25285 (1)	0.95168 (7)	2.62 (1)
C(7)	0.5351 (3)	0.32123 (5)	0.7003 (2)	1.82 (3)
C(8)	0.6369 (3)	0.36258 (5)	0.6372 (2)	1.53 (3)
C(9)	0.8418 (3)	0.38369 (4)	0.7545 (2)	1.28 (2)
5-Nitrosaccharin				
O(1*W*)	0.41147 (7)	0.2447 (2)	0.3038 (2)	1.34 (2)
Na$^+$	0.49956 (5)	0.5000	0.4898 (2)	1.06 (1)
S(1)	0.37884 (2)	0.7717 (1)	0.97837 (6)	0.934 (5)
O(11)	0.44414 (5)	0.7512 (2)	1.2030 (2)	1.18 (2)
O(12)	0.38622 (8)	0.9546 (2)	0.8214 (3)	1.35 (2)
N(2)	0.37580 (7)	0.5831 (2)	0.7766 (3)	1.24 (2)
C(3)	0.29657 (7)	0.4977 (2)	0.7693 (3)	1.22 (2)
O(3)	0.27588 (8)	0.3549 (2)	0.6204 (3)	1.85 (2)
C(4)	0.23568 (7)	0.5942 (2)	0.9654 (3)	1.17 (2)
C(5)	0.15084 (8)	0.5447 (2)	1.0098 (3)	1.37 (2)
C(6)	0.10898 (7)	0.6615 (2)	1.2027 (3)	1.35 (2)
N(6)	0.01779 (7)	0.6212 (3)	1.2484 (3)	1.75 (2)
O(61)	−0.01967 (9)	0.5049 (4)	1.0895 (4)	2.67 (3)
O(62)	−0.0166 (1)	0.7090 (4)	1.4402 (5)	2.99 (4)
C(7)	0.14738 (8)	0.8178 (2)	1.3493 (3)	1.44 (2)
C(8)	0.23251 (7)	0.8681 (2)	1.3000 (3)	1.31 (2)
C(9)	0.27414 (6)	0.7513 (2)	1.1062 (2)	0.99 (2)
6-Nitrosaccharin				
O(1*W*)	0.4927 (1)	0.4105 (2)	0.7273 (2)	2.89 (4)
O(2*W*)	0.4570 (1)	0.0705 (3)	0.3081 (2)	3.47 (5)
O(3*W*1)	0.6158 (3)	0.1014 (5)	−0.0018 (5)	1.83 (8)
O(3*W*2)	0.6281 (2)	0.1791 (5)	−0.0398 (5)	1.66 (8)
O(4*W*1)	0.6836 (2)	0.2402 (4)	0.3959 (4)	2.58 (8)

Table 2 (*cont.*)

	x	*y*	*z*	U_{eq}
O(4*W*2)	0.6792 (2)	0.1996 (4)	0.2775 (4)	2.00 (7)
Na^+	0.49461 (6)	0.2597 (1)	0.4840 (1)	3.02 (3)
S(1)	−0.13679 (4)	0.87638 (9)	0.67978 (8)	3.12 (2)
O(11)	−0.1580 (1)	0.9391 (2)	0.4919 (2)	3.09 (4)
O(12)	−0.1022 (1)	1.0173 (3)	0.7398 (3)	5.12 (6)
N(2)	−0.2420 (1)	0.7972 (3)	0.8297 (2)	3.44 (6)
C(3)	−0.2162 (2)	0.6058 (4)	0.9143 (3)	3.75 (7)
O(3)	−0.2814 (1)	0.5094 (3)	1.0353 (2)	5.11 (6)
C(4)	−0.0978 (1)	0.5144 (3)	0.8468 (3)	3.04 (6)
C(5)	−0.0434 (2)	0.3250 (4)	0.9094 (3)	3.30 (6)
C(6)	0.0684 (2)	0.2752 (4)	0.8298 (3)	3.48 (7)
C(7)	0.1196 (1)	0.4151 (3)	0.6897 (3)	3.68 (7)
N(7)	0.2375 (1)	0.3589 (3)	0.6057 (3)	4.85 (7)
O(71)	0.2926 (1)	0.2167 (3)	0.6938 (3)	6.28 (8)
O(72)	0.2750 (1)	0.4573 (3)	0.4521 (4)	8.22 (9)
C(8)	0.0674 (1)	0.6056 (3)	0.6226 (4)	3.55 (7)
C(9)	−0.0425 (1)	0.6496 (3)	0.7091 (3)	3.04 (6)

Table 3. *Common bond distances* (Å) *in the saccharin derivatives*

	4-Methoxysaccharin (1)	4-Methoxysaccharin (2)	5-Chloro-saccharin	5-Nitro-saccharin	6-Nitro-saccharin
S(1)—O(11)	1.442 (3)	1.445 (3)	1.454 (1)	1.450 (1)	1.445 (2)
S(1)—O(12)	1.440 (3)	1.445 (3)	1.457 (1)	1.455 (2)	1.441 (2)
S(1)—N(2)	1.610 (4)	1.598 (3)	1.595 (1)	1.599 (2)	1.621 (2)
S(1)—C(9)	1.771 (4)	1.761 (4)	1.767 (1)	1.767 (1)	1.775 (2)
N(2)—C(3)	1.349 (5)	1.357 (5)	1.364 (2)	1.362 (2)	1.346 (3)
C(3)—O(3)	1.231 (5)	1.231 (4)	1.243 (2)	1.235 (2)	1.240 (3)
C(3)—C(4)	1.504 (5)	1.502 (5)	1.503 (2)	1.506 (2)	1.510 (2)
C(4)—C(5)	1.396 (5)	1.394 (5)	1.392 (2)	1.387 (2)	1.384 (3)
C(4)—C(9)	1.381 (5)	1.387 (5)	1.391 (2)	1.382 (2)	1.382 (3)
C(5)—C(6)	1.400 (5)	1.389 (5)	1.398 (2)	1.394 (2)	1.397 (3)
C(6)—C(7)	1.378 (6)	1.390 (6)	1.399 (2)	1.391 (2)	1.386 (3)
C(7)—C(8)	1.380 (6)	1.374 (7)	1.398 (2)	1.397 (2)	1.387 (3)
C(8)—C(9)	1.382 (5)	1.379 (5)	1.390 (2)	1.394 (2)	1.384 (2)

The atomic numbering scheme is nearly identical for all compounds. One exception is 4-methoxysaccharin which has two formula units together with three methanol molecules in the asymmetric unit. Therefore the first digit in the atom numbers of 4-methoxysaccharin is the number of the anion. Details can be seen in Fig. 1.

The four structures differ in the substituents on the benzene ring, in the positions of the Na cations, and the positions and the type of the solvent molecules. The crystal structures of 5-chloro- and 5-nitrosaccharin are very similar (same Na^+ coordination, same hydrogen bonds). In 5-chlorosaccharin the Na cations lie on inversion centers so that two independent Na coordination polyhedra exist.

In comparing the bond distances of all five independent molecules it has to be kept in mind that the experimental conditions for 4-methoxysaccharin were different from those for the other compounds. With the exception of the bond lengths near the substituents most bond lengths are the same in the different compounds within two standard deviations (Table 3).

The average values of the N(2)—C(3) and C(3)—O(3) bond lengths are 1.356 and 1.236 Å. The corresponding values of the sweet 4-hydroxysaccharin (Rudert, Buschmann, Luger, Gregson & Trummlitz, 1988) are 1.356 (1) and 1.245 (1) Å. The average values of some salts of saccharin, which are sweet with a bitter by-taste, are 1.350 and 1.237 Å [Na^+ and Mg^{2+} salts: Jovanovski & Kamenar (1982); $2K^+.Na^+$ salt: Malik, Haider, Hossain & Hursthouse (1984)]. So the bond length C(3)—O(3) in 4-hydroxysaccharin is slightly larger than in the bitter compounds and in saccharin, which was indirectly predicted by CNDO/2 calculations. To test if this is not caused by different crystal structures one may compare the isostructural compounds 5-chloro- (bitter, slightly sweet by-taste) and 5-nitrosaccharin (bitter). The corresponding bond lengths are 1.364 (2)/1.362 (2) and 1.243 (2)/1.235 (2) Å.

Correlation coefficients between bond lengths in the five-membered ring and taste (ranging from 0 for

Table 4. *Common bond angles* (°) *in the saccharin derivatives*

	4-Methoxysaccharin (1)	4-Methoxysaccharin (2)	5-Chloro-saccharin	5-Nitro-saccharin	6-Nitro-saccharin
O(11)—S(1)—O(12)	114.8 (2)	114.1 (2)	113.03 (6)	113.05 (8)	115.8 (1)
O(11)—S(1)—N(2)	112.5 (2)	111.3 (2)	112.23 (6)	111.58 (8)	110.2 (1)
O(11)—S(1)—C(9)	109.9 (2)	110.9 (2)	111.38 (6)	111.56 (6)	110.5 (1)
O(12)—S(1)—N(2)	110.3 (2)	112.0 (2)	111.17 (6)	112.11 (8)	111.2 (1)
O(12)—S(1)—C(9)	111.0 (2)	110.2 (2)	110.18 (6)	109.63 (7)	110.7 (1)
N(2)—S(1)—C(9)	97.1 (2)	97.1 (2)	97.89 (6)	97.95 (6)	96.9 (1)
S(1)—N(2)—C(3)	111.6 (3)	112.4 (3)	111.62 (9)	111.2 (1)	111.6 (1)
N(2)—C(3)—O(3)	122.8 (3)	122.6 (3)	124.4 (1)	124.3 (1)	124.7 (2)
N(2)—C(3)—C(4)	113.4 (3)	112.4 (3)	112.9 (1)	113.0 (1)	113.5 (2)
O(3)—C(3)—C(4)	123.8 (3)	124.9 (3)	122.8 (1)	122.7 (1)	121.8 (2)
C(3)—C(4)—C(5)	130.5 (3)	131.0 (3)	128.0 (1)	128.0 (1)	128.4 (2)
C(3)—C(4)—C(9)	111.0 (3)	111.2 (3)	111.2 (1)	111.4 (1)	111.1 (2)
C(5)—C(4)—C(9)	118.5 (3)	117.8 (3)	120.7 (1)	120.6 (1)	120.5 (2)
C(4)—C(5)—C(6)	118.3 (3)	118.6 (3)	116.5 (1)	115.8 (1)	118.2 (2)
C(5)—C(6)—C(7)	120.7 (4)	121.4 (4)	122.7 (1)	124.1 (1)	119.1 (2)
C(6)—C(7)—C(8)	122.0 (4)	121.1 (4)	120.3 (1)	119.6 (1)	124.2 (2)
C(7)—C(8)—C(9)	116.1 (4)	116.4 (4)	116.7 (1)	116.2 (1)	114.6 (2)
S(1)—C(9)—C(4)	106.8 (3)	106.9 (3)	106.30 (9)	106.32 (8)	106.9 (1)
S(1)—C(9)—C(8)	128.9 (3)	128.4 (3)	130.6 (1)	129.9 (1)	129.7 (2)
C(4)—C(9)—C(8)	124.2 (3)	124.7 (4)	123.0 (1)	123.7 (1)	123.4 (2)

Table 5. *Other bond distances* (Å) *and angles* (°)

4-Methoxysaccharin			
C(15)—O(15)	1.357 (5)	C(25)—O(25)	1.362 (5)
O(15)—C(151)	1.431 (6)	O(25)—C(251)	1.439 (6)
C(14)—C(15)—O(15)	118.1 (3)	C(24)—C(25)—O(25)	117.9 (3)
O(15)—C(15)—C(16)	123.6 (3)	O(25)—C(25)—C(26)	123.5 (4)
C(15)—O(15)—C(151)	118.0 (3)	C(25)—O(25)—C(251)	116.9 (3)
O(1*M*)—C(1*M*)	1.419 (6)	O(2*M*)—C(2*M*)	1.427 (5)
O(3*M*)—C(3*M*)	1.381 (8)		
5-Chlorosaccharin			
C(6)—Cl(6)	1.738 (2)		
C(5)—C(6)—Cl(6)	119.1 (1)	Cl(6)—C(6)—C(7)	118.1 (1)
5-Nitrosaccharin			
C(6)—N(6)	1.470 (2)	N(6)—O(62)	1.230 (3)
N(6)—O(61)	1.224 (3)		
C(5)—C(6)—N(6)	118.1 (1)	C(6)—N(6)—O(62)	118.1 (2)
N(6)—C(6)—C(7)	117.8 (1)	O(61)—N(6)—O(62)	124.0 (1)
C(6)—N(6)—O(61)	117.9 (1)		
6-Nitrosaccharin			
C(7)—N(7)	1.477 (2)	N(7)—O(72)	1.218 (3)
N(7)—O(71)	1.222 (3)		
C(6)—C(7)—N(7)	118.3 (2)	C(7)—N(7)—O(72)	118.3 (2)
N(7)—C(7)—C(8)	117.5 (2)	O(71)—N(7)—O(72)	123.3 (2)
C(7)—N(7)—O(71)	118.4 (2)		

bitter to 1 for sweet) were calculated. This included 4-hydroxysaccharin and saccharin sodium salt (Jovanovski & Kamenar, 1982). The bonds S(1)—C(9), C(3)—C(4) and C(4)—C(9), which are nearest to the six-membered ring, have the highest correlations (−0.700, −0.659, 0.450) followed by C(3)—O(3) (0.395).

The ring systems of all the molecules are nearly planar. The angles between the benzene ring and the isothiazolone ring are 2.6 (2)/1.3 (1) [methoxysaccharin molecules (1)/(2)], 3.76 (4) (5-chlorosaccharin), 1.84 (5) (5-nitrosaccharin) and 3.25 (8)° (6-nitrosaccharin).

The shape of the benzene ring is influenced by the substituents. The participating bond angles C—C—C (Table 4) can be compared with those of unsubstituted sodium saccharinate [values found by Jovanovski & Kamenar (1982) follow in square brackets]: 4-methoxysaccharin, 118.5 (3) [118.2 (3)]; 5-chlorosaccharin/5-nitrosaccharin, 122.7 (1)/124.0 (1) [121.2 (2)]; 6-nitrosaccharin, 124.2 (2)° [121.1 (2)°].

All solvent molecules take part in medium-strong hydrogen bonds (Table 6). There are no intramolecular hydrogen bonds and only one intermolecular weak one between anions (4-methoxysaccharin). Most of the solvent molecules are coordinated to one or two Na cations. In all four compounds and in 4-hydroxysaccharin, the carbonyl O atom, the isothiazolone N atom and the SO_2 group each take

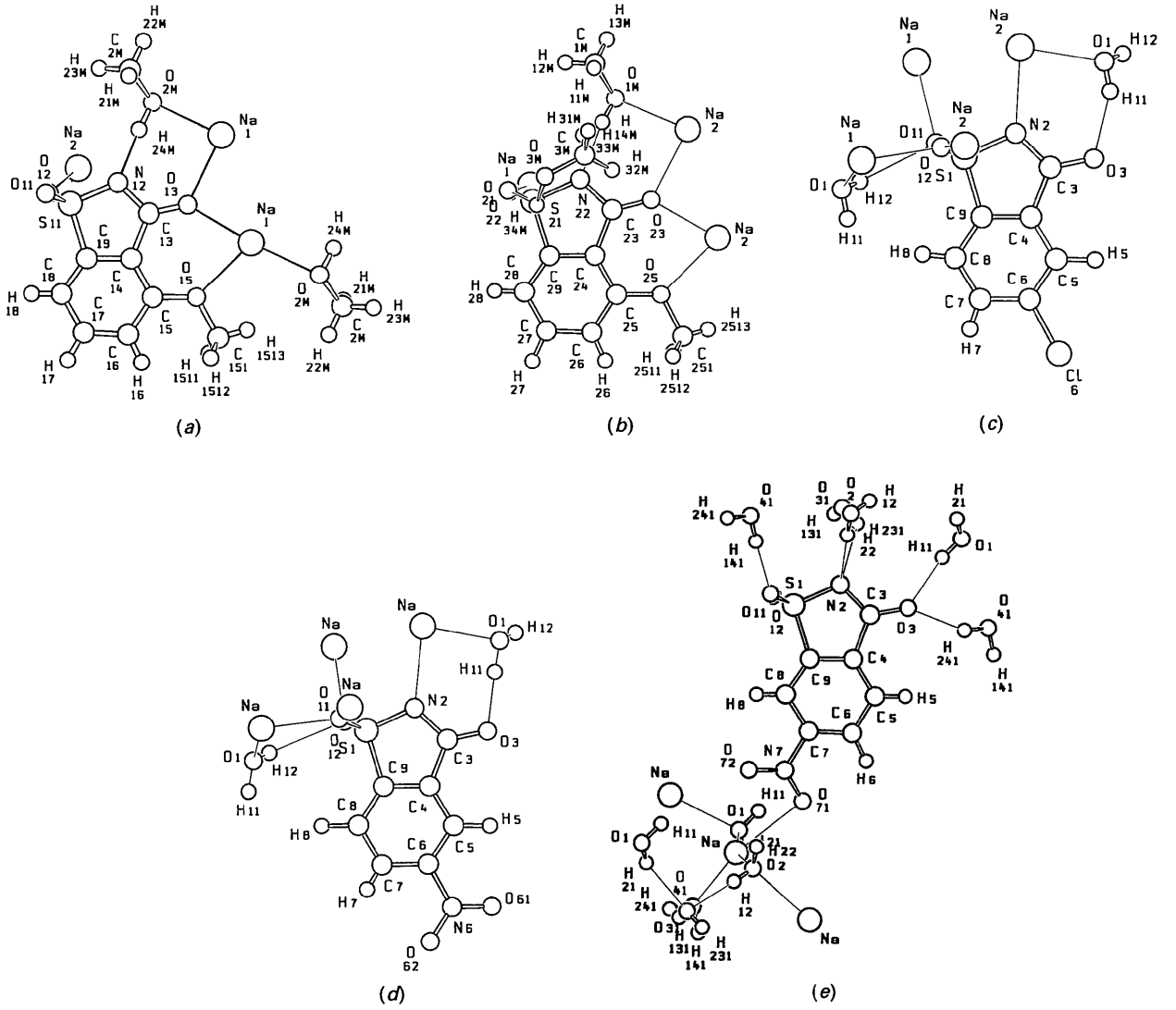

Fig. 1. *SCHAKAL*88 drawings (Keller, 1988) of the asymmetric units with the addition of hydrogen bonds and Na^+ coordinations. (*a*) 4-Methoxysaccharin [anion (1)]. (*b*) 4-Methoxysaccharin [anion (2)]. (*c*) 5-Chlorosaccharin. (*d*) 5-Nitrosaccharin. (*e*) 6-Nitrosaccharin.

Table 6. *Hydrogen-bond distances* (Å)

X···Y		Symmetry operation for Y*	X···Y		Symmetry operation for Y*
4-Methoxysaccharin					
O(1*M*)···N(22)	2.742 (4)	(*b*)	O(3*M*)···O(21)	2.807 (6)	(*a*)
O(2*M*)···N(12)	2.750 (3)	(*b*)	C(151)···O(11)	3.423 (7)	(*c*)
5-Chlorosaccharin					
O(1*W*)···O(11)	3.068 (2)	(*a*)	O(1*W*)···O(3)	2.757 (2)	(*d*)
5-Nitrosaccharin					
O(1*W*)···O(12)	3.035 (2)	(*e*)	O(1*W*)···O(3)	2.743 (2)	(*a*)
6-Nitrosaccharin					
O(1*W*)···O(3)	2.852 (2)	(*f*)	O(4*W*1)···O(3)	2.857 (3)	(*k*)
O(1*W*)···O(3*W*1)	3.001 (4)	(*g*)	O(1*W*)···O(3*W*2)	2.720 (4)	(*g*)
O(2*W*)···O(3*W*1)	2.663 (4)	(*a*)	O(2*W*)···O(3*W*2)	2.992 (3)	(*a*)
O(2*W*)···N(2)	3.041 (2)	(*b*)	O(3*W*2)···N(2)	3.143 (4)	(*h*)
O(3*W*1)···O(4*W*2)	2.798 (6)	(*a*)	O(4*W*2)···O(11)	2.935 (3)	(*l*)
O(3*W*1)···N(2)	2.871 (4)	(*h*)	O(4*W*2)···O(3)	2.520 (3)	(*k*)
O(4*W*1)···O(11)	2.658 (3)	(*j*)			

* For symmetry codes see Table 7.

Table 7. Na^+*-coordination distances* (Å)

X···Y		Symmetry operation for Y*	X···Y		Symmetry operation for Y*
4-Methoxysaccharin					
Na^+(1)···O(22)	2.352 (3)	(*a*)	Na^+(2)···O(12)	2.394 (3)	(*a*)
Na^+(1)···O(13)	2.309 (3)	(*a*)	Na^+(2)···O(23)	2.321 (3)	(*a*)
Na^+(1)···O(15)	2.448 (3)	(*a*)	Na^+(2)···O(25)	2.482 (3)	(*a*)
Na^+(1)···O(13)	2.385 (3)	(*b*)	Na^+(2)···O(23)	2.430 (2)	(*m*)
Na^+(1)···O(1*M*)	2.505 (3)	(*a*)	Na^+(2)···O(1*M*)	2.449 (3)	(*n*)
Na^+(1)···O(2*M*)	2.424 (3)	(*a*)	Na^+(2)···O(2*M*)	2.425 (3)	(*n*)
5-Chlorosaccharin					
Na^+(1)···O(11)	2.422 (1)	(*o*)	Na^+(2)···O(12)	2.396 (1)	(*a*)
Na^+(1)···O(12)	2.333 (1)	(*a*)	Na^+(1)···O(1*W*)	2.356 (1)	(*a*)
Na^+(2)···N(2)	2.438 (1)	(*o*)	Na^+(2)···O(1*W*)	2.414 (1)	(*g*)
5-Nitrosaccharin					
Na^+···O(12)	2.378 (2)	(*p*)	Na^+···O(11)	2.377 (1)	(*r*)
Na^+···O(11)	2.327 (1)	(*q*)	Na^+···O(1*W*)	2.359 (1)	(*a*)
Na^+···N(2)	2.469 (2)	(*a*)	Na^+···O(1*W*)	2.351 (1)	(*s*)
6-Nitrosaccharin					
Na^+···O(1*W*)	2.411 (2)	(*a*)	Na^+···O(4*W*1)	2.313 (3)	(*a*)
Na^+···O(1*W*)	2.477 (2)	(*m*)	Na^+···O(4*W*2)	2.478 (3)	(*a*)
Na^+···O(2*W*)	2.389 (3)	(*a*)	Na^+···O(71)	2.691 (2)	(*a*)
Na^+···O(2*W*)	2.485 (2)	(*t*)			

Symmetry operations: (*a*) x, y, z; (*b*) $-x, 1-y, 1-z$; (*c*) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (*d*) $-1+x, y, -1+z$; (*e*) $x, -1+y, -1+z$; (*f*) $-x, 1-y, 2-z$; (*g*) $x, y, 1+z$; (*h*) $1+x, -1+y, -1+z$; (*j*) $1+x, -1+y, z$; (*k*) $1+x, y, -1+z$; (*l*) $1+x, -1+y, z$; (*m*) $1-x, 1-y, 1-z$; (*n*) $1+x, y, z$; (*o*) $-1+x, y, z$; (*p*) $1-x, -\frac{1}{2}+y, 1-z$; (*q*) $x, y, -1+z$; (*r*) $1-x, -\frac{1}{2}+y, 2-z$; (*s*) $1-x, \frac{1}{2}+y, 1-z$; (*t*) $1-x, -y, 1-z$.

part in hydrogen bonds or Na coordinations. These parts of the molecules are believed to be involved in hydrogen bridges with receptors which are responsible for sweet and bitter taste.

Each of the Na cations is coordinated sixfold by O atoms or O and N atoms which form distorted octahedra (Table 7). The distortions (*i.e.* average distance between the coordinated atoms and the corresponding points of a regular octahedron divided by the radius of the octahedron) range from 0.069 in 5-nitrosaccharin to 0.188 in 5-chlorosaccharin.

In 5-chloro- and 5-nitrosaccharin the molecules form a system of layers ...($A'BA$)($A'BA$)(A'..., where the layers A and A' consist of saccharin anions and layer B of Na cations and water molecules (Fig. 2). The substituents are near the plane between A and A'. A and A' are packed in a way that avoids close contact between substituents of neighbouring layers, presumably because of electrostatic repulsion.

In 5-chlorosaccharin the glide plane is between A and A'. The distance of the Cl atoms from the plane is 0.084 (3) Å, the distances from each other are 4.139 (4) and 4.288 (4) Å. In 5-nitrosaccharin the bc plane at $x = 0$ is between A and A'. The distance of

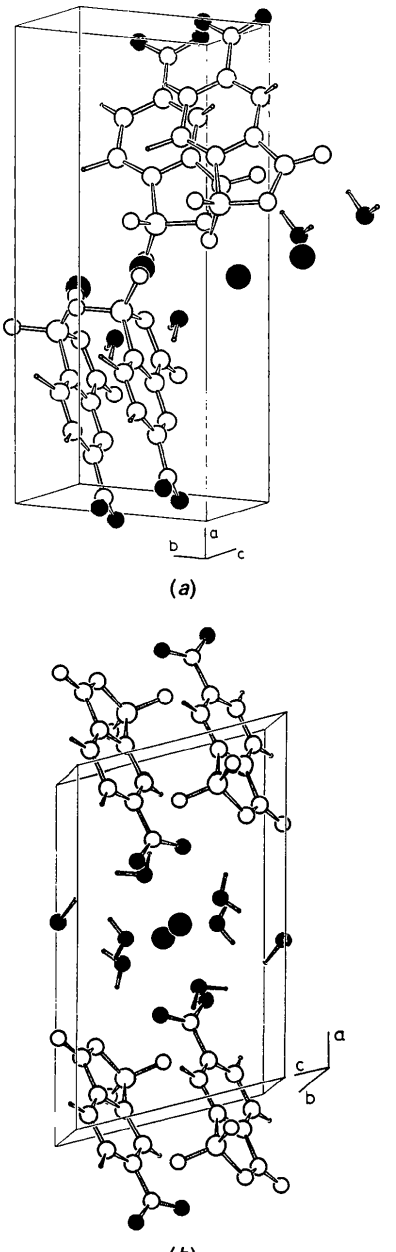

Fig. 2. *SCHAKAL*88 drawings of the cells of (*a*) 5-nitro- and (*b*) 6-nitrosaccharin. The Na^+ cations, the water and the nitro O atoms are shown as filled circles.

O(61) from this plane is 0.298 (2) Å, that of O(62) is 0.258 (2) Å. The distances between O(61) in *A* and O(62) in *A'* are 3.285 (9) and 3.394 (8) Å. Each nitro O atom dips into the neighbouring layer in order to get closer to the positively charged N atom N(7).

In 6-nitrosaccharin all Na cations and water molecules form a layer with the plane (0.5 *y*, *z*) in the middle and with a thickness of about 5 Å (Fig. 2*b*). The Na cations are situated near an axis (0.5, *y*, 0.5) at a distance of 0.1466 (8) Å.

Concluding remarks

The results do not confirm the predicted correlation between the C(3)—O(3) bond length and taste quality. If there is such a correlation the corresponding variation of the bond length should be smaller than 1%. Each of the compounds including 4-hydroxysaccharin has a different anion surrounding (except for the almost isostructural 5-chloro- and 5-nitrosaccharin), so that no characteristic interaction pattern for sweet- or bitter-tasting species can be recognized. No correlation between hydrogen bonds and Na coordination on one hand and taste quality on the other can be seen.

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Structure at 293 and 135 K of β-Tetrakis[bis(ethylenedithio)tetrathiafulvalene] Tetracyanoplatinate(II): β-[BEDT-TTF]$_4$[Pt(CN)$_4$]

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Abstract

$[C_{10}H_8S_8]_4[Pt(CN)_4]$, $M_r = 1837.9$. At 293 K: triclinic, $P\bar{1}$, $a = 9.721$ (7), $b = 11.127$ (6), $c = 16.552$ (8) Å, $\alpha = 76.90$ (5), $\beta = 81.52$ (5), $\gamma = 62.88$ (5)°, $V = 1550$ Å^3, $Z = 1$, $D_x = 1.969$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 33.64$ cm^{-1}, $F(000) = 914$, $R = 0.043$ based on 4192 observed reflections with $I \geq 6\sigma(I)$. At 135 K: triclinic, $P\bar{1}$, $a = 9.693$ (4), $b = 10.890$ (4), $c = 16.521$ (5) Å, $\alpha = 77.12$ (3), $\beta = 81.84$ (4), $\gamma = 62.70$ (3)°, $V = 1509$ Å^3, $Z = 1$, $D_x = 2.022$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 34.55$ cm^{-1}, $F(000) = 914$, $R = 0.062$ based on 4107 observed reflections with $I \geq 6\sigma(I)$. One carbon (C7 and C16) of the terminal ethylenic groups of each independent

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