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Saccharin, redetermined at 120 K: a three-dimensional hydrogen-bonded framework

James L. Wardell,[a] John N. Low[b] and Christopher Glidewell[c]*

[a]Instituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil, [b]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [c]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland

Correspondence e-mail: cg@st-andrews.ac.uk

Key indicators
Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.039
wR factor = 0.092
Data-to-parameter ratio = 15.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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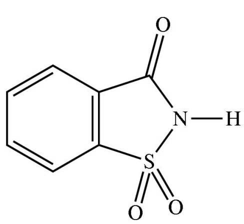
Molecules of the title compound, $C_7H_5NO_3S$, are linked by paired N—H···O=C hydrogen bonds into $R_2^2(8)$ dimers and these dimers are linked into a three-dimensional framework structure by a combination of three independent C—H···O hydrogen bonds.

Comment

The structure of saccharin, (I), was determined some years ago (Bart, 1968; Okaya, 1969) using diffraction data collected at ambient temperature, and accordingly the precision of some of the interatomic distances is fairly modest. While in one report (Bart, 1968) the precision on the bond angles is satisfactory, in the other (Okaya, 1969) no s.u. values were quoted for the interbond angles. The molecules were reported to form centrosymmetric dimers constructed from paired N—H···O=C hydrogen bonds.



(I)

We have now taken the opportunity to redetermine this structure using diffraction data collected at 120 (2) K; this has permitted refinement to a rather lower R factor and has provided interatomic distances of significantly higher precision (Fig. 1 and Table 1). The cell dimensions and space group indicate that the same phase is present at 120 K as at ambient temperature.

The molecules are linked by a combination of N—H···O and C—H···O hydrogen bonds in which all three O atoms act as acceptors (Table 2). The N—H···O hydrogen bond, which utilizes a carbonyl O atom as acceptor, generates a centrosymmetric $R_2^2(8)$ dimer (Fig. 2), exactly as reported previously; for the sake of convenience, the reference molecule has been selected so that this dimer lies across ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). These dimers are linked into a single three-dimensional framework by three independent C—H···O hydrogen bonds, each utilizing a different O atom as acceptor (Table 2). The hydrogen bond involving C2 as donor links the $R_2^2(8)$ dimer centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) to those centred at ($-\frac{1}{2}$, 0, 0), ($-\frac{1}{2}$, 1, 0), ($\frac{3}{2}$, 0, 1) and ($\frac{3}{2}$, 1, 1), thereby generating a ($-$102) sheet. The hydrogen bond involving C4 as the donor links the ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) dimer to those centred at ($\frac{1}{2}$, $-$1, 0), ($\frac{1}{2}$, $-$1, 1), ($\frac{1}{2}$, 2, 0) and ($\frac{1}{2}$, 2, 1), so forming a (100) sheet. This sheet is reinforced by the third, rather

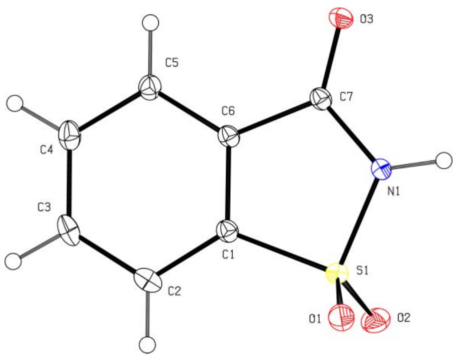


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoid are drawn at the 30% probability level.

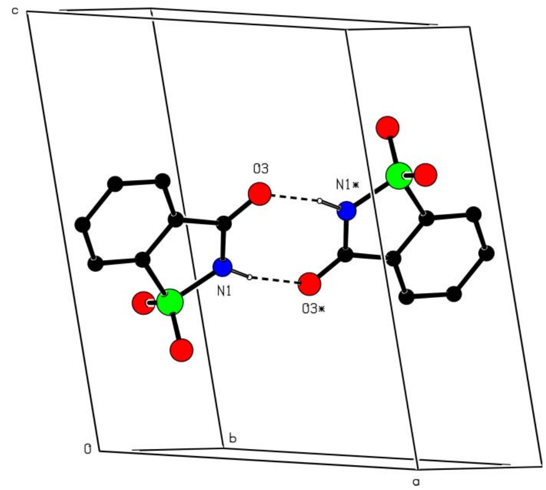


Figure 2
Part of the crystal structure of (I), showing the formation of an $R_2^2(8)$ dimer. For clarity, H atoms bonded to C atoms have been omitted. Hydrogen bonds are indicated by dashed lines. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

weak, C—H···O hydrogen bond where C5 is the donor; this interaction links the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ dimer to those centred at $(\frac{1}{2}, 0, 0)$, $(\frac{1}{2}, 1, 0)$, $(\frac{1}{2}, 0, 1)$ and $(\frac{1}{2}, 1, 1)$, so that the (100) sheet is of considerable complexity. The combination of the (100) and $(\bar{1}02)$ sheets suffices to link all of the molecules into a single framework.

The original reports on the structure of (I) (Bart, 1968; Okaya, 1969) made no mention of the C—H···O hydrogen bonds; at the time of those reports, the notion that such interactions could be of structural significance was not widely recognized and certainly not widely accepted.

Experimental

Crystals of compound (I) suitable for single-crystal X-ray diffraction were grown from an ethanol solution.

Crystal data

$C_7H_5NO_3S$
$M_r = 183.18$
Monoclinic, $P2_1/c$
$a = 9.4722$ (4) Å
$b = 6.9227$ (2) Å
$c = 11.7322$ (3) Å
$\beta = 103.203$ (3)°
$V = 748.98$ (4) Å^3
$Z = 4$
$D_x = 1.624$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1706 reflections
$\theta = 3.6$–27.5°
$\mu = 0.39$ mm^{-1}
$T = 120$ (2) K
Lath, colourless
0.44 × 0.16 × 0.11 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.847$, $T_{max} = 0.958$
12303 measured reflections
1706 independent reflections
1490 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 27.5°$
$h = -11 \rightarrow 12$
$k = -8 \rightarrow 9$
$l = -14 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.092$
$S = 1.11$
1706 reflections
109 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0203P)^2 + 0.8656P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—O1	1.4291 (15)	C1—C2	1.387 (3)
S1—O2	1.4323 (15)	C2—C3	1.393 (3)
S1—N1	1.6643 (16)	C3—C4	1.390 (3)
S1—C1	1.7560 (19)	C4—C5	1.392 (3)
N1—C7	1.374 (2)	C5—C6	1.382 (3)
C7—O3	1.223 (2)	C6—C1	1.391 (3)
C7—C6	1.481 (3)		
O1—S1—O2	117.37 (9)	S1—N1—C7	115.65 (13)
O1—S1—N1	110.37 (9)	O3—C7—N1	124.53 (17)
O2—S1—N1	109.48 (9)	O3—C7—C6	126.12 (17)
O1—S1—C1	111.71 (9)	N1—C7—C6	109.34 (16)
O2—S1—C1	112.68 (9)	S1—C1—C6	110.01 (14)
N1—S1—C1	92.41 (8)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3^{i}	0.95	1.86	2.786 (2)	167
C2—H2···O2^{ii}	0.95	2.46	3.377 (3)	161
C4—H4···O1^{iii}	0.95	2.55	3.375 (2)	145
C5—H5···O3^{iv}	0.95	2.50	3.169 (2)	128

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

All H atoms were located in difference maps and then treated as riding atoms with C—H = 0.95 Å and N—H = 0.95 Å, and with U_{iso}(H) = 1.2 U_{eq}(C,N).

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *WinGX* (Farrugia, 1999) and *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JLW thanks CNPq and FAPERJ for financial support.

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Saccharin

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$C_7H_5NO_3S$
M_r = 183.18
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 9.4722 (4) Å
b = 6.9227 (2) Å
c = 11.7322 (3) Å
β = 103.203 (3)°
V = 748.98 (4) Å^3
Z = 4
$F(000)$ = 376
D_x = 1.624 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1706 reflections
θ = 3.6–27.5°
μ = 0.39 mm^{-1}
T = 120 K
Lath, colourless
0.44 × 0.16 × 0.11 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: Bruker–Nonius FR91 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
T_{min} = 0.847, T_{max} = 0.958
12303 measured reflections
1706 independent reflections
1490 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 27.5°, θ_{min} = 3.6°
h = −11→12
k = −8→9
l = −14→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.092
S = 1.11
1706 reflections
109 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0203P)^2 + 0.8656P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.63 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	0.21067 (5)	0.22909 (7)	0.34594 (4)	0.01955 (15)

O1	0.24538 (17)	0.1705 (2)	0.23876 (12)	0.0271 (3)
O2	0.08217 (15)	0.3423 (2)	0.33788 (13)	0.0287 (4)
O3	0.52054 (15)	0.3079 (2)	0.60463 (11)	0.0216 (3)
N1	0.35108 (18)	0.3420 (2)	0.43105 (14)	0.0207 (4)
C1	0.2223 (2)	0.0356 (3)	0.44441 (16)	0.0184 (4)
C2	0.1361 (2)	−0.1284 (3)	0.43285 (18)	0.0256 (4)
C3	0.1685 (2)	−0.2627 (3)	0.52349 (19)	0.0271 (5)
C4	0.2818 (2)	−0.2340 (3)	0.62062 (18)	0.0256 (4)
C5	0.3685 (2)	−0.0699 (3)	0.62963 (17)	0.0218 (4)
C6	0.3373 (2)	0.0646 (3)	0.54037 (15)	0.0170 (4)
C7	0.4147 (2)	0.2483 (3)	0.53308 (16)	0.0177 (4)
H1	0.3838	0.4622	0.4087	0.025*
H2	0.0588	−0.1481	0.3664	0.031*
H3	0.1117	−0.3767	0.5188	0.033*
H4	0.3004	−0.3275	0.6815	0.031*
H5	0.4470	−0.0508	0.6953	0.026*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0205 (3)	0.0188 (3)	0.0173 (2)	−0.00189 (18)	0.00002 (17)	−0.00062 (17)
O1	0.0372 (9)	0.0252 (8)	0.0189 (7)	−0.0036 (6)	0.0067 (6)	−0.0018 (6)
O2	0.0221 (8)	0.0307 (8)	0.0303 (8)	0.0049 (6)	−0.0002 (6)	0.0014 (6)
O3	0.0239 (7)	0.0222 (7)	0.0169 (6)	−0.0054 (6)	0.0008 (5)	−0.0016 (5)
N1	0.0235 (9)	0.0165 (8)	0.0195 (8)	−0.0048 (6)	−0.0003 (6)	0.0015 (6)
C1	0.0204 (9)	0.0176 (9)	0.0176 (9)	−0.0012 (7)	0.0053 (7)	−0.0021 (7)
C2	0.0225 (10)	0.0275 (11)	0.0264 (10)	−0.0062 (9)	0.0048 (8)	−0.0070 (9)
C3	0.0307 (11)	0.0191 (10)	0.0349 (11)	−0.0085 (8)	0.0146 (9)	−0.0033 (8)
C4	0.0344 (12)	0.0202 (10)	0.0253 (10)	−0.0029 (8)	0.0130 (9)	0.0015 (8)
C5	0.0279 (10)	0.0196 (9)	0.0186 (9)	−0.0012 (8)	0.0067 (8)	0.0001 (7)
C6	0.0197 (9)	0.0161 (9)	0.0159 (8)	−0.0010 (7)	0.0056 (7)	−0.0034 (7)
C7	0.0197 (9)	0.0168 (9)	0.0174 (9)	−0.0017 (7)	0.0057 (7)	−0.0027 (7)

Geometric parameters (Å, º)

S1—O1	1.4291 (15)	C2—C3	1.393 (3)
S1—O2	1.4323 (15)	C2—H2	0.95
S1—N1	1.6643 (16)	C3—C4	1.390 (3)
S1—C1	1.7560 (19)	C3—H3	0.95
N1—C7	1.374 (2)	C4—C5	1.392 (3)
N1—H1	0.9462	C4—H4	0.95
C7—O3	1.223 (2)	C5—C6	1.382 (3)
C7—C6	1.481 (3)	C5—H5	0.95
C1—C2	1.387 (3)	C6—C1	1.391 (3)
O1—S1—O2	117.37 (9)	C1—C2—C3	116.72 (18)
O1—S1—N1	110.37 (9)	C1—C2—H2	121.6
O2—S1—N1	109.48 (9)	C3—C2—H2	121.6

O1—S1—C1	111.71 (9)	C4—C3—C2	121.65 (19)
O2—S1—C1	112.68 (9)	C4—C3—H3	119.2
N1—S1—C1	92.41 (8)	C2—C3—H3	119.2
S1—N1—C7	115.65 (13)	C3—C4—C5	120.71 (19)
C7—N1—H1	123.4	C3—C4—H4	119.6
S1—N1—H1	120.9	C5—C4—H4	119.6
O3—C7—N1	124.53 (17)	C6—C5—C4	118.18 (18)
O3—C7—C6	126.12 (17)	C6—C5—H5	120.9
N1—C7—C6	109.34 (16)	C4—C5—H5	120.9
C2—C1—C6	122.17 (18)	C5—C6—C1	120.57 (18)
C2—C1—S1	127.80 (15)	C5—C6—C7	126.84 (17)
S1—C1—C6	110.01 (14)	C1—C6—C7	112.59 (16)

O1—S1—N1—C7	−113.64 (15)	C1—C2—C3—C4	−0.1 (3)
O2—S1—N1—C7	115.70 (15)	C2—C3—C4—C5	−0.9 (3)
C1—S1—N1—C7	0.60 (16)	C3—C4—C5—C6	1.0 (3)
S1—N1—C7—O3	178.42 (15)	C4—C5—C6—C1	−0.1 (3)
S1—N1—C7—C6	−0.3 (2)	C4—C5—C6—C7	179.60 (18)
O1—S1—C1—C2	−66.2 (2)	C2—C1—C6—C5	−1.0 (3)
O2—S1—C1—C2	68.4 (2)	S1—C1—C6—C5	−179.60 (15)
N1—S1—C1—C2	−179.26 (19)	C2—C1—C6—C7	179.32 (18)
O1—S1—C1—C6	112.34 (14)	S1—C1—C6—C7	0.7 (2)
O2—S1—C1—C6	−113.01 (14)	O3—C7—C6—C5	1.3 (3)
N1—S1—C1—C6	−0.72 (15)	N1—C7—C6—C5	−179.96 (18)
C6—C1—C2—C3	1.1 (3)	O3—C7—C6—C1	−178.97 (19)
S1—C1—C2—C3	179.43 (16)	N1—C7—C6—C1	−0.3 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O3^{i}	0.95	1.86	2.786 (2)	167
C2—H2···O2^{ii}	0.95	2.46	3.377 (3)	161
C4—H4···O1^{iii}	0.95	2.55	3.375 (2)	145
C5—H5···O3^{iv}	0.95	2.50	3.169 (2)	128

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*, *y*−1/2, −*z*+1/2; (iii) *x*, −*y*−1/2, *z*+1/2; (iv) −*x*+1, *y*−1/2, −*z*+3/2.