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Hydrogen-bonded dimers in *N*-(2-nitrophenylthio)saccharin

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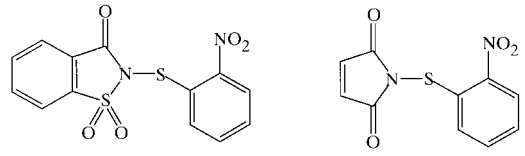
In the title compound, 2-(2-nitrophenylthio)-1,2-benzothiazol-3(2*H*)-one 1,1-dioxide, 2-$O_2NC_6H_4S(C_7H_4NO_3S)$ or $C_{13}H_8N_2O_5S_2$, the planes of the saccharin and nitrophenylthiolate portions are almost orthogonal. The molecules are linked by C—H···O═S hydrogen bonds [C···O 3.308 (3) Å, H···O 2.44 Å and C—H···O 155°] into cyclic centrosymmetric $R_2^2(16)$ dimers, reinforced by aromatic $\pi\cdots\pi$ stacking interactions between the nitrated aryl rings.

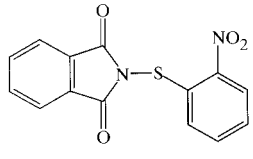
Comment

We have recently discussed the interplay between molecular conformation and intermolecular forces, particularly soft hydrogen bonds of the C—H···O type, in a range of 2-nitrophenylthiolates of type 2-$O_2NC_6H_4SX$ (Low, Storey *et al.*, 2000; Low, Glidewell & Wardell, 2000; Glidewell *et al.*, 2000). We report here an investigation of *N*-(2-nitrophenylthio)-saccharin, (I), selected for study because of the incorporation



(I)

(II)



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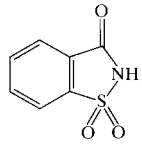

(IV)

in its structure of three different groups, namely CO, NO_2 and SO_2, known to be good acceptors of C—H···O hydrogen bonds. In a previous paper (Low, Storey *et al.*, 2000), we reported the structure of the pyrrolidinedione derivative (II), clearly related to (I), in which both carbonyl O atoms and one of the two nitro O atoms act as acceptors of C—H···O hydrogen bonds; similarly, in the phthalimido analogue (III) (Iwasaki & Masuko, 1986), the same three O atoms act as acceptors. In both (II) and (III), the C—H···O hydrogen bonds link the molecules into continuous sheets, albeit in entirely different ways (Low, Storey *et al.*, 2000).

The overall molecular conformation of (I) (Fig. 1) closely resembles those observed previously for (II) and (III). Both the nitro group and the α atom of the *X* substituent are nearly coplanar with the nitrated aryl ring, while the plane of the heterocyclic component is almost orthogonal (Table 1). The near orthogonality of these planes must be ascribed to the mutually repulsive effect of the lone pairs on S and N normal to these two planes, which themselves seek to become orthogonal in order to minimize their mutual overlap and

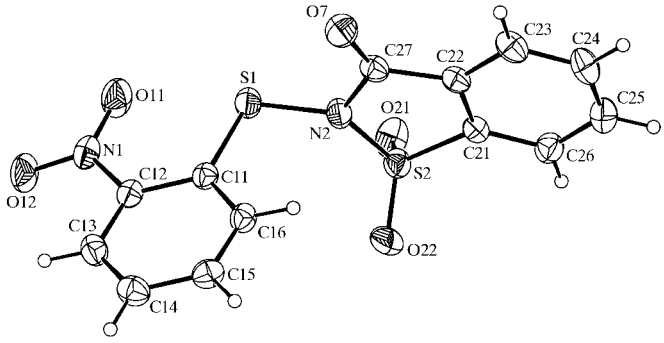

Figure 1
The asymmetric unit of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

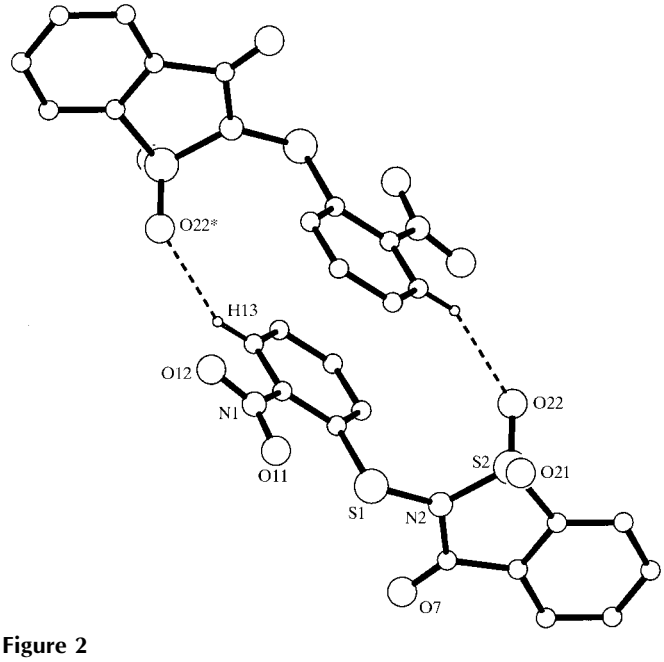

Figure 2
Part of the crystal structure of (I) showing the formation of a cyclic centrosymmetric dimer. For the sake of clarity, H atoms not involved in dimer formation have been omitted. The atom marked with an asterisk (*) is at the symmetry position $(2-x, 1-y, -z)$.

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resonance integrals. The sum of the bond angles at N2 in the heterocyclic ring is almost 360°; within this ring, the internal angle at S2 is extremely small for four-coordinate S^{VI} and it is very much smaller than the mean internal angles, 108°, in a planar five-membered ring. Neither (II) nor (III) show any peculiarities in the internal ring angles, but in saccharin itself, (IV) (Okaya, 1969), the internal angle at S is 92.2° (no s.u. given). The idealized internal angles in this ring, which contains three trigonal C, one planar trigonal N and a four-coordinate S atom, sum to *ca* 590°, some 50° greater than the maximum possible for such a ring. It is evident that the S atom makes the greatest contribution to the relief of bond-angle strain in this ring, followed by the carbonyl C27 atom (Table 1).

The N—C and N—S bond lengths within the heterocyclic ring are both very much shorter than the mean values for their types, 1.414 and 1.688 Å, respectively (Allen *et al.*, 1987); similarly, the C27—O7 distance is closer to the mean values observed in four-membered rings (1.198 Å in cyclobutanones and 1.198 Å in β-lactams) than to those in five-membered rings (1.208 Å in cyclopentanones and 1.225 Å in γ-lactams). The corresponding values observed in (IV) were 1.369 (5), 1.663 (4) and 1.214 (5) Å, respectively (Okaya, 1969).

The surprising feature of the crystal structure of (I) is the comparative paucity of hydrogen bonds (Table 2). A single C—H···O hydrogen bond links the molecules into cyclic centrosymmetric dimers based on an $R_2^2(16)$ motif (Bernstein *et al.*, 1995) (Fig. 2). Neither the carbonyl nor the nitro O atoms in (I) act as hydrogen-bond acceptors, in sharp contrast to the behaviour of the corresponding atoms in (II) and (III). The hydrogen bonds forming the dimers are reinforced by aromatic $\pi\cdots\pi$-stacking interactions between the two nitrated aryl rings within the dimer; the planes of the parallel aryl rings at (x, y, z) and ($2-x$, $1-y$, $-z$) are *ca* 3.47 Å apart and the ring centroids are offset by *ca* 1.41 Å, ideal for the development of these interactions. Doubtless the near planarity of the 2-$O_2NC_6H_4SN<$ fragment is conducive to the occurrence of these interactions. There are, however, no such interactions involving the saccharin portion of the molecule.

The formation of finite dimers in (I) may be contrasted with the extensive intermolecular hydrogen bonding in saccharin itself, (IV), where there are hard hydrogen bonds of the N—H···O═C type linking pairs of molecules into cyclic $R_2^2(8)$ dimers (Okaya, 1969). In addition, although not mentioned in the original report, there are rather strong C—H···O═S hydrogen bonds [C···O 3.383 Å, H···O 2.46 Å and C—H···O 164° (s.u.'s uncertain)] linking the molecules into continuous sheets built from $R_6^6(30)$ rings (Fig. 3). Each individual molecule is hydrogen bonded to three others, while each $R_2^2(8)$ dimer is hydrogen bonded to four others; thus, the description of the net topology (Batten & Robson, 1998) differs depending upon whether monomers or dimers are taken to be the nodes of the net. For monomer nodes, the net is of the (6,3) type, while for dimer nodes, the net is of the (4,4) type.

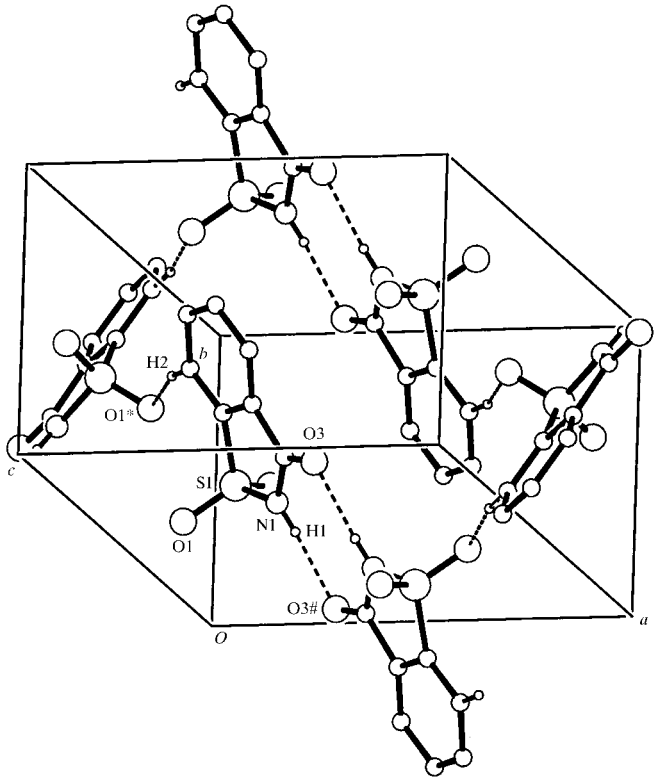

Figure 3
Part of the crystal structure of (IV) showing the formation of one of the $R_6^6(30)$ rings making up the (6,3) net. Atom labelling is as in Okaya (1969). For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions ($-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) and ($1-x$, $-y$, $1-z$), repectively.

Experimental

A sample of compound (I) was obtained from Aldrich. Crystals suitable for single-crystal X-ray diffraction analysis were grown from an ethanol solution.

Crystal data

$C_{13}H_8N_2O_5S_2$
M_r = 336.33
Monoclinic, *C*2/*c*
a = 23.6968 (15) Å
b = 7.6510 (5) Å
c = 15.1664 (10) Å
β = 92.3600 (10)°
V = 2747.4 (3) Å^3
Z = 8
D_x = 1.626 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2420 reflections
θ = 2.68–25.00°
μ = 0.414 mm^{-1}
T = 298 (2) K
Plate, yellow
0.35 × 0.25 × 0.10 mm

Data collection

KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.869, T_{max} = 0.960
8477 measured reflections
2420 independent reflections
1740 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 25°
$h = -28 \rightarrow 28$
$k = -9 \rightarrow 8$
$l = -18 \rightarrow 17$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.081
S = 0.921
2420 reflections
199 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0445P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—O11	1.227 (3)	S2—N2	1.6876 (19)
N1—O12	1.216 (2)	C27—N2	1.414 (3)
N1—C12	1.452 (3)	S2—O21	1.4195 (17)
S1—C11	1.777 (2)	S2—O22	1.4206 (18)
S1—N2	1.7072 (18)	S2—C21	1.745 (2)
N2—S1—C11	101.04 (10)	S2—N2—C27	115.17 (14)
O11—N1—O12	123.1 (2)	N2—S2—C21	92.45 (9)
O21—S2—O22	117.98 (11)	S2—C21—C22	110.95 (16)
S1—N2—S2	119.09 (11)	C21—C22—C27	113.75 (19)
S1—N2—C27	123.81 (15)	C22—C27—N2	107.67 (18)
C12—C11—S1—N2	−172.72 (16)	C11—S1—N2—S2	95.94 (14)
C11—C12—N1—O11	−8.0 (3)	C11—S1—N2—C27	−100.68 (19)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C13—H13···O22^{i}	0.93	2.44	3.308 (3)	155

Symmetry code: (i) $2-x, 1-y, -z$.

Compound (I) crystallized in the monoclinic system; space group *C*2/*c* or *Cc* from the systematic absences. *C*2/*c* was assumed and confirmed by the analysis. H atoms were treated as riding atoms with C—H = 0.93 Å and O—H = 0.82 Å. Examination of the structure with *PLATON* (Spek, 2000) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *XPREP* (Bruker, 1997); cell refinement: *XPREP*; data reduction: *XPREP*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Aberdeen using a Bruker SMART 1000 diffractometer. The authors thank Dr W. T. A. Harrison for all his help and advice.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1418). Services for accessing these data are described at the back of the journal.

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