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Conformational preferences and supramolecular aggregation in 2-nitrophenylthiolates: 2-nitrophenyl-β-D-thiogalactopyranoside

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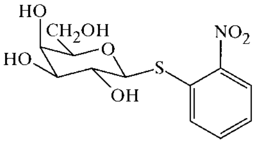
In the title compound, $C_{12}H_{15}NO_7S$, the molecular conformation shows a concerted disrotatory twist of the nitro group and the galactose fragment out of the plane of the aryl ring. The molecules are linked by O—H···O hydrogen bonds [O···O range 2.725 (2)–3.024 (2) Å and O—H···O range 155–175°] to form a three-dimensional framework.

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, $2\text{-}O_2NC_6H_4SX$ (Low, Storey *et al.*, 2000; Low, Glidewell & Wardell, 2000; Glidewell *et al.*, 2000). Two distinct conformational types can be observed in this series of compounds: in one conformation, corresponding to the global energy minimum, both the nitro group and the α atom of substituent X are effectively coplanar with the nitrated aryl ring; the second conformer, in which the nitro group and the X substituent exhibit a significant and concerted twist out of the aryl ring plane, represents a local energy minimum and seems to occur only in the presence of intermolecular hydrogen bonds. As a further test of this idea, we report here a structural investigation of 2-nitrophenyl-β-D-thiogalactopyranoside, (I), selected for study because of the potential of the galactose fragment to form multiple intermolecular O—H···O hydrogen bonds.



(I)

The nitro group in (I) (Fig. 1) is twisted out of the plane of the adjacent aryl ring and this is accompanied by the usual (Low, Storey *et al.*, 2000; Low, Glidewell & Wardell, 2000; Glidewell *et al.*, 2000) disrotatory twist of the S substituent out of this plane, as illustrated by the torsion angles C11—C12—N1—O11 and C12—C11—S1—C21 (Table 1). The extensive hydrogen bonding described below involves the nitro O11 atom as one of the hydrogen-bond acceptors. The β-D-galactopyranoside fragment adopts the usual chair conformation (Longchambon *et al.*, 1975; Sheldrick, 1976), with all substituents other than O4 in equatorial sites.

The bond lengths in the nitroaryl ring portion (Table 1) do not show the marked quinonoid bond fixation observed in $2\text{-}O_2NC_6H_4SCH{=}CHPh$ (Low, Storey *et al.*, 2000). The C—O bond lengths in the galactose fragment show the usual difference between C21—O5 and C25—O5; the exocyclic C—O bonds span the range 1.4151 (17)–1.4358 (17) Å, whereas in β-D-galactopyranose itself, the exocyclic C—O bond distances are all of similar lengths, apart from the hemiacetal bond at C1 (Sheldrick, 1976).

The molecules of (I) are linked by four different hydrogen bonds: O3 is both a hydrogen-bond donor and a double acceptor, O6 is both a donor and an acceptor, O4 is a donor only and the nitro O11 atom is a single acceptor (Table 2). Each molecule acts as a hydrogen-bond donor to three others and as a hydrogen-bond acceptor from three further molecules, and the overall supramolecular structure takes the form of a three-dimensional framework, which is best analysed in terms of the interaction of the individual motifs parallel to [100], [010] and [001]. Atoms O4 and O6 in the molecule at (x, y, z) both act as donor to O3 in the molecule at $(-\frac{1}{2}+x, \frac{3}{2}-y, 1-z)$, while O4 and O6 at $(-\frac{1}{2}+x, \frac{3}{2}-y, 1-z)$, in turn, are donors to O3 at $(-1+x, y, z)$, and propagation of these interactions produces a spiral chain generated by the 2_1 screw axis along $(x, \frac{3}{4}, \frac{1}{2})$. The O4 and O6 donors individually generate $C(5)$ and $C(7)$ (Bernstein *et al.*, 1995) spirals along [100]; embedded in the spiral chains are $R^1_2(8)$ rings. At the same time, O2 in the molecule at (x, y, z) acts as donor to O6 at $(1 + x, y, z)$, so producing by translation

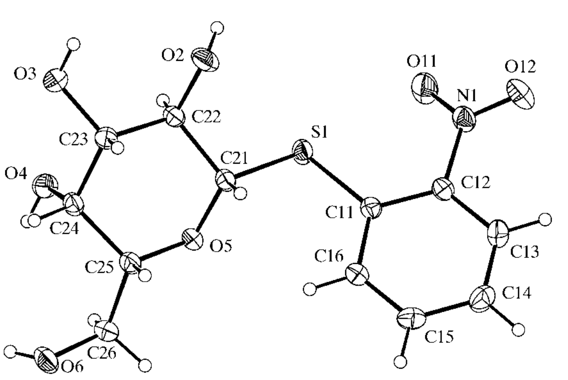


Figure 1
The asymmetric unit of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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a $C(8)$ chain parallel to [100]. The combination of this chain with the $C(5)$ spiral generates a chain of fused $R_3^3(16)$ rings parallel to [100] (Fig. 2)

Atom O3 at (x, y, z) is itself a hydrogen-bond donor to O11 at $(2 - x, \frac{1}{2} + y, \frac{3}{2} - z)$, while O3 at $(2 - x, \frac{1}{2} + y, \frac{3}{2} - z)$ is a donor to O11 at $(x, 1 + y, z)$; this hydrogen bond thus produces a $C(10)$ spiral parallel to [010] generated by the 2_1 screw axis along $(1, y, \frac{3}{4})$ (Fig. 3). The combination of the two types of spiral along [100] and [010], respectively, generates a third type of spiral, a $C_2^2(15)$ chain parallel to [001], in which alternate molecules act as donors and double acceptors of hydrogen bonds (Fig. 4). The [100] and [010] spirals can each be constructed using a single type of hydrogen bond; concurrent use of these two types generates the [001] spiral. By means of these three motifs parallel to [100], [010] and [001], the molecule at (x, y, z) is linked to those at $(\pm 1 + x, y, z)$, $(x, \pm 1 + y, z)$ and $(x, y, \pm 1 + z)$, so that a single framework is sufficient to define the entire crystal structure.

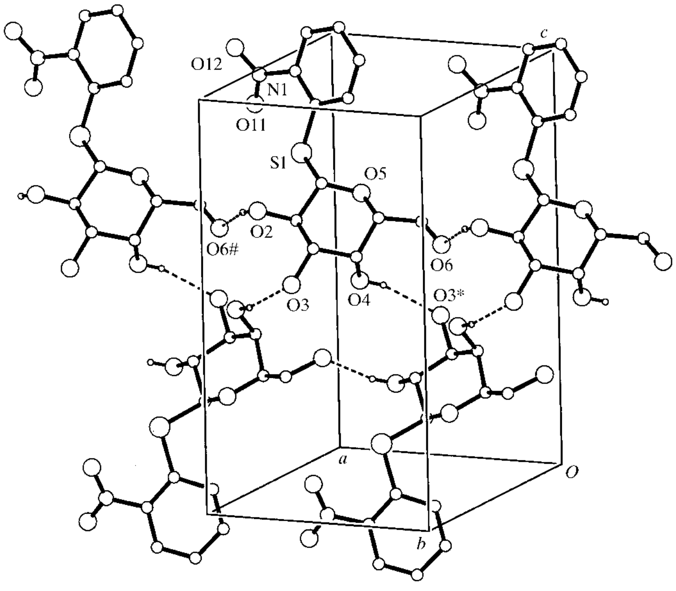

Figure 2
Part of the crystal structure of (I) showing a chain of fused $R_3^3(16)$ rings parallel to [100]. For the sake of clarity, only the H atoms involved in the motif shown are drawn. The atoms marked with an asterisk (*) and hash (#) are at the symmetry positions $(-\frac{1}{2} + x, \frac{3}{2} - y, 1 - z)$ and $(1 + x, y, z)$, respectively.

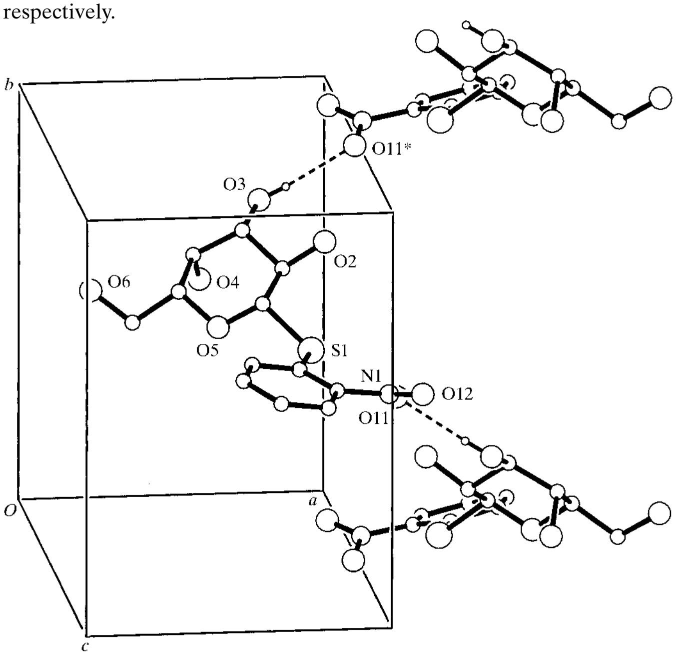

Figure 3
Part of the crystal structure of (I) showing a $C(10)$ spiral parallel to [010]. For the sake of clarity, only the H atoms involved in this motif are shown. The atom marked with an asterisk (*) is at the symmetry position $(2 - x, \frac{1}{2} + y, \frac{3}{2} - z)$.

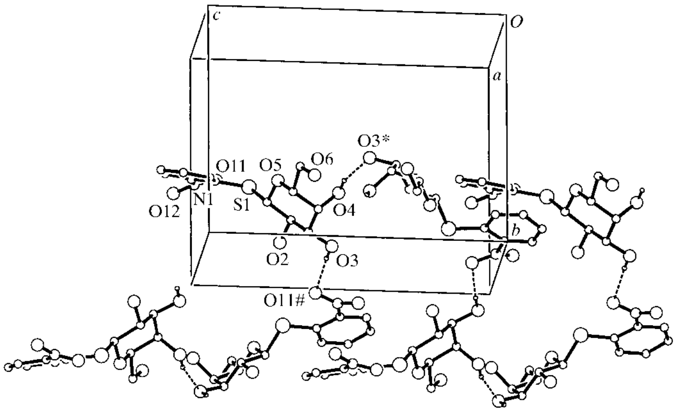

Figure 4
Part of the crystal structure of (I) showing a $C_2^2(15)$ spiral parallel to [001]. For the sake of clarity, only the H atoms involved in this motif are shown. The atoms marked with an asterisk (*) and hash (#) are at the symmetry positions $(-\frac{1}{2} + x, \frac{3}{2} - y, 1 - z)$ and $(2 - x, \frac{1}{2} + y, \frac{3}{2} - z)$, respectively.

Experimental

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

Crystal data

$C_{12}H_{15}NO_7S$
$M_r = 317.31$
Orthorhombic, $P2_12_12_1$
$a = 8.2214\ (4)$ Å
$b = 11.4293\ (5)$ Å
$c = 14.3861\ (6)$ Å
$V = 1351.79\ (10)$ Å^3
$Z = 4$
$D_x = 1.559$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 3097 reflections
$\theta = 2.27$–$27.44°$
$\mu = 0.274$ mm^{-1}
$T = 298\ (2)$ K
Block, yellow
$0.37 \times 0.30 \times 0.30$ mm

Data collection

KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min} = 0.905$, $T_{max} = 0.922$
10 075 measured reflections
1780 independent reflections (plus 1317 Friedel-related reflections)

2874 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 27.44°$
$h = -10 \rightarrow 7$
$k = -14 \rightarrow 14$
$l = -18 \rightarrow 18$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.074$
$S = 1.011$
3097 reflections
188 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0510P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.03 (6)

Table 1
Selected geometric parameters (Å, °).

C11—C12	1.4013 (19)	C21—O5	1.4205 (16)
C12—C13	1.387 (2)	C22—O2	1.4151 (17)
C13—C14	1.369 (3)	C23—O3	1.4358 (17)
C14—C15	1.388 (2)	C24—O4	1.4255 (18)
C15—C16	1.384 (2)	C25—O5	1.4412 (16)
C16—C11	1.401 (2)	C26—O6	1.4186 (19)
C12—N1	1.464 (2)	S1—C11	1.7628 (14)
N1—O11	1.2215 (18)	S1—C21	1.8086 (14)
N1—O12	1.2250 (18)		
C11—S1—C21	102.73 (7)	O11—N1—O12	123.35 (15)
C21—S1—C11—C12	−155.93 (12)	O5—C21—C22—C23	56.89 (15)
C11—C12—N1—O11	−27.3 (2)	C21—C22—C23—C24	−53.32 (15)
C11—S1—C21—O5	−85.82 (10)	C22—C23—C24—C25	52.23 (16)
C11—S1—C21—C22	154.44 (10)	C23—C24—C25—O5	−55.14 (16)
S1—C21—C22—C23	176.28 (9)	C24—C25—O5—C21	61.34 (15)
S1—C21—O5—C25	−179.18 (9)	C25—O5—C21—C22	−61.72 (14)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O6^{i}	0.82	1.93	2.725 (2)	163
O3—H3···O11^{ii}	0.82	2.18	3.000 (2)	175
O4—H4···O3^{iii}	0.82	2.20	2.989 (2)	161
O6—H6···O3^{iii}	0.82	2.26	3.024 (2)	155

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

Compound (I) crystallized in the orthorhombic system; space group $P2_12_12_1$ was assigned uniquely from the systematic absences. H atoms were treated as riding atoms, with C—H = 0.93–0.98 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: SK1419). Services for accessing these data are described at the back of the journal.

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