

4-Iodo-*N,N*-bis(2-nitrophenylsulfonyl)-aniline: a three-dimensional framework structure built from six independent C—H···O hydrogen bonds

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In the title compound [systematic name: 4-iodophenylimino bis(2-nitrobenzenesulfinate)], C₁₈H₁₂IN₃O₈S₂, where the molecules do not exhibit even approximate local symmetry, the molecules are linked into a complex three-dimensional structure by six independent C—H···O hydrogen bonds, which utilize O atoms in nitro and sulfonyl groups as the acceptors.

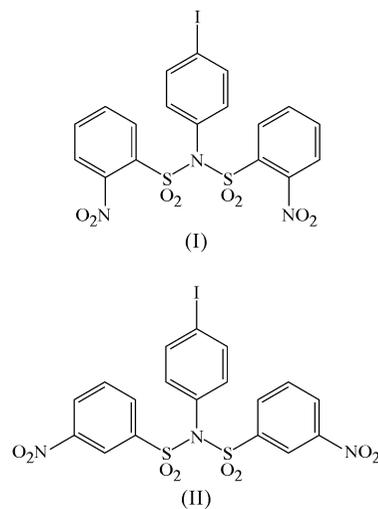
Comment

We report here the structure of 4-iodo-*N,N*-bis(2-nitrophenylsulfonyl)aniline, (I) (Fig. 1), where the supramolecular aggregation proves to be markedly different from that in the isomeric compound 4-iodo-*N,N*-bis(3-nitrophenylsulfonyl)aniline, (II), which was reported recently as part of a wider study of intermolecular interactions in iodonitroarenesulfonamides (Kelly *et al.*, 2002). In (II), the molecules lie across twofold rotation axes in the space group *C2/c*, and they are linked into sheets by a combination of a C—H···O=S hydrogen bond and a three-centre iodo-sulfonyl interaction, but the nitro O atoms play no role in the intermolecular aggregation.

In (I), the molecules have a planar coordination at atom N1. The molecular conformation is defined by eight torsion angles (Table 1), and these show that the molecules do not exhibit even approximate rotational symmetry; in particular, the orientations of the nitrated aryl rings and the nitro groups are very different for the two independent 2-nitrophenylsulfonyl units within the molecule.

There are no iodo-nitro or iodo-sulfonyl interactions nor aromatic π - π stacking interactions in the structure of (I); instead, the molecules are linked into a complex three-

dimensional framework by a combination of six independent C—H···O hydrogen bonds (Table 2). However, the formation of the structure of (I) can be analysed in terms of three one-dimensional substructures.



In the first substructure, which is built from the two shortest hydrogen bonds, atoms C13 and C14 in the molecule at (*x*, *y*, *z*) act as donors, respectively, to atoms O21 and O22 in the molecules at (*x*, *y*, 1 + *z*) and (1 − *x*, 1 − *y*, 2 − *z*), and propagation by translation and inversion of these two hydrogen bonds generates a chain of edge-fused rings running parallel to the [001] direction, with $R_2^2(18)$ rings (Bernstein *et al.*, 1995) centred at ($\frac{1}{2}$, $\frac{1}{2}$, *n*) (*n* = zero or integer) and $R_4^4(14)$ rings centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ + *n*) (*n* = zero or integer) (Fig. 2).

The second substructure depends solely on inversion operations. Atoms C2 and C15 in the molecule at (*x*, *y*, *z*) act as hydrogen-bond donors, respectively, to nitro atoms O221 and O222 in the molecule at (1 − *x*, 1 − *y*, 1 − *z*), so forming a

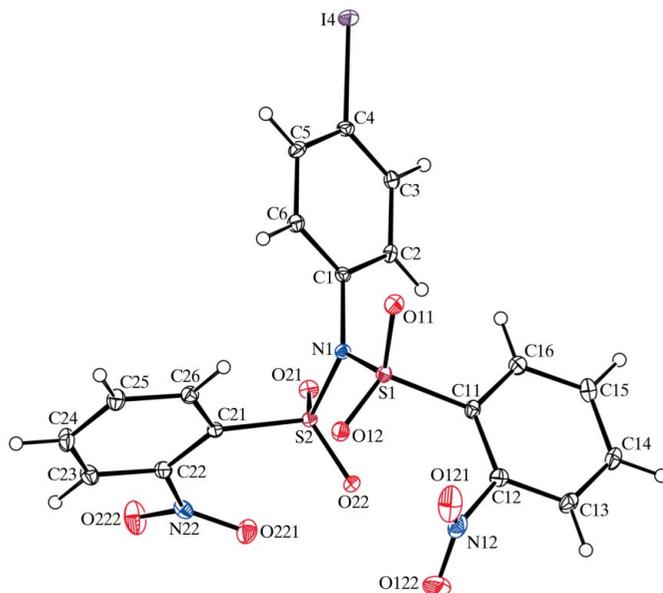


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

centrosymmetric motif in which an $R_2^2(22)$ ring surrounds an $R_2^2(18)$ ring (Fig. 3). At the same time, atom C26 at (x, y, z) acts as a hydrogen-bond donor to sulfonyl atom O11 in the molecule at $(-x, 1 - y, 1 - z)$, so forming a centrosymmetric $R_2^2(14)$ motif. Propagation by inversion of these three hydrogen bonds generates a chain of edge-fused rings running parallel to the $[100]$ direction, with $R_2^2(18)$ and $R_2^2(22)$ rings centred at $(\frac{1}{2} + n, \frac{1}{2}, \frac{1}{2})$ ($n = \text{zero or integer}$) and $R_2^2(14)$ rings centred at $(n, \frac{1}{2}, \frac{1}{2})$ ($n = \text{zero or integer}$) (Fig. 4).

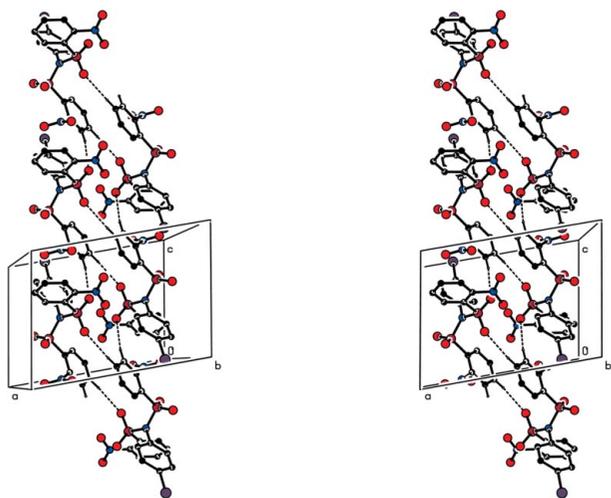


Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded chain along $[001]$ built from alternating $R_2^2(18)$ and $R_4^4(14)$ rings. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

The combination of the $[001]$ and $[100]$ chains (Figs. 2 and 4) generates a sheet lying parallel to (010) and occupying the domain $\frac{1}{4} < y < \frac{3}{4}$; a second sheet, related to the first by the action of the translational symmetry elements, occupies the domain $-\frac{1}{4} < y < \frac{1}{4}$, and the action of the third and final one-dimensional substructure is to link adjacent (010) sheets. Atom C23 in the molecule at (x, y, z) , which forms part of the sheet in the domain $\frac{1}{4} < y < \frac{3}{4}$, acts as a hydrogen-bond donor to sulfonyl atom O22 in the molecule at $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$, which itself forms part of the sheet in the domain $-\frac{1}{4} < y < \frac{1}{4}$. Hence, propagation of this hydrogen bond produces a $C(6)$ chain running parallel to the $[010]$ direction and generated by the

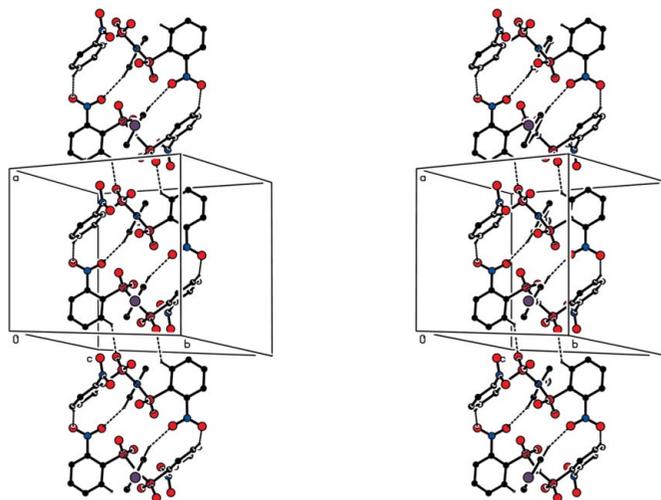


Figure 4
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded chain along $[100]$ built from $R_2^2(18)$ and $R_2^2(22)$ rings alternating with $R_4^4(14)$ rings. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

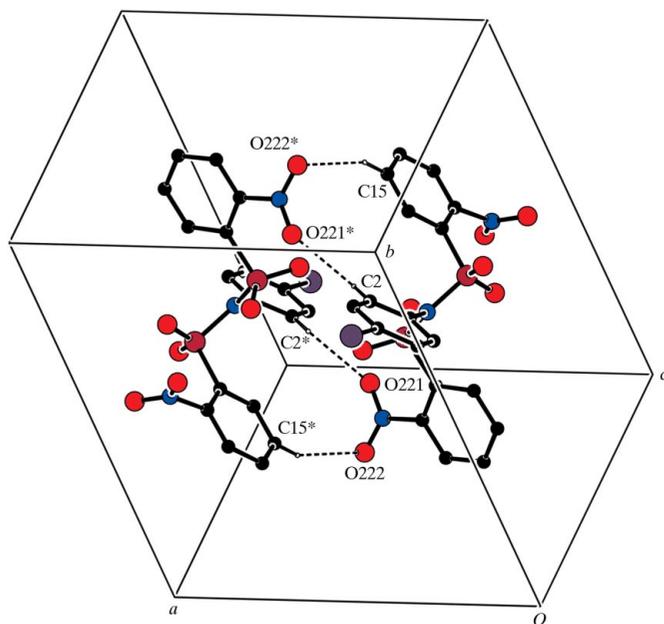


Figure 3
Part of the crystal structure of (I), showing the formation of two concentric ring motifs. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

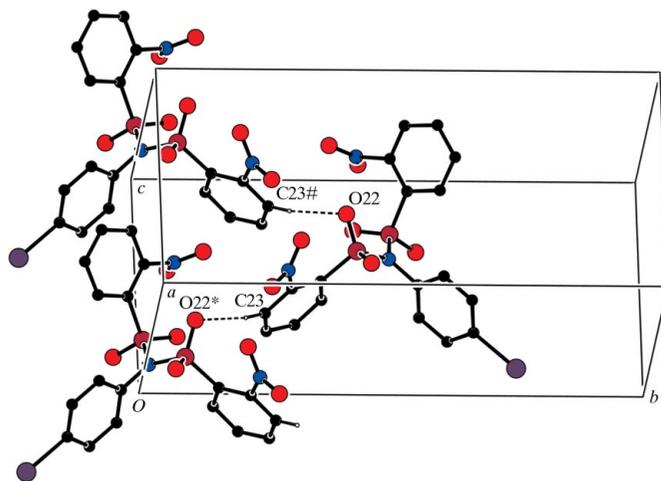


Figure 5
Part of the crystal structure of (I), showing the formation of a $C(6)$ hydrogen-bonded chain along $[010]$, which links adjacent (010) sheets. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ and $(x, \frac{1}{2} - y, \frac{1}{2} + z)$, respectively.

c-glide plane at $y = \frac{1}{4}$ (Fig. 5), whose effect is to link adjacent (010) sheets, thereby forming a continuous three-dimensional framework structure.

The C—H...O hydrogen bonds in (I) (Table 2) utilize three of the four sulfonyl O atoms as acceptors, with atom O22 acting as a double acceptor; while both O atoms of one of the nitro groups are employed as hydrogen-bond acceptors, those in the other nitro group play no role in the supramolecular aggregation. In almost all respects, therefore, the direction-specific intermolecular interactions in isomers (I) and (II) are different, leading to markedly different supramolecular structures.

Experimental

A solution of 2-nitrophenylsulfonyl chloride (1.11 g, 5 mmol), 4-iodoaniline (0.55 g 2.5 mmol) and triethylamine (2 ml) in 1,2-dichloroethane (20 ml) was heated under reflux for 0.5 h; the mixture was then cooled and the solvent was removed under reduced pressure. The solid product was purified by column chromatography on alumina using ethyl acetate as the eluant and then recrystallized from ethanol [m.p. 494–495 K (decomposition)]. NMR (CDCl₃): δ (H) 6.76 (*d*, 2H, *J* = 8.9 Hz) and 7.75 (*d*, *J* = 8.9 Hz) (C₆H₄I group), 7.63 (*dd*, 2H, *J* = 7.9 and 1.4 Hz), 7.74 (*dt*, 2H, *J* = 7.9 and 1.4 Hz), 7.79 (*dt*, 2H, *J* = 7.9 and 1.4 Hz), 8.22 (*dd*, 2H, *J* = 7.9 and 1.4 Hz) (C₆H₄NO₂ groups); IR (KBr disk, cm⁻¹): 1537, 1479, 1464, 1442, 1389, 1367, 1269, 1199, 1169, 1145, 1122, 1057, 1009, 958, 930, 900, 850, 807, 778, 740, 698, 653, 612, 586, 535, 414.

Crystal data

C₁₈H₁₂IN₃O₈S₂
M_r = 589.33
 Monoclinic, *P*₂₁/*c*
a = 12.1680 (2) Å
b = 18.6695 (4) Å
c = 9.0443 (2) Å
 β = 100.030 (2)°
V = 2023.20 (7) Å³

Z = 4
D_x = 1.935 Mg m⁻³
 Mo *K*α radiation
 μ = 1.84 mm⁻¹
T = 120 (2) K
 Block, colourless
 0.10 × 0.10 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
T_{min} = 0.837, *T_{max}* = 0.837

27333 measured reflections
 4612 independent reflections
 3902 reflections with *I* > 2σ(*I*)
R_{int} = 0.054
 θ_{\max} = 27.5°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.029
wR (*F*²) = 0.067
S = 1.08
 4612 reflections
 289 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 0.9151P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.88 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.99 \text{ e } \text{Å}^{-3}$

The space group *P*₂₁/*c* was uniquely determined from the systematic absences. All H atoms were located in difference maps and then treated as riding atoms, with C—H distances of 0.95 Å and *U*_{iso}(H) values of 1.2*U*_{eq}(C).

Table 1

Selected bond and torsion angles (°).

S1—N1—S2	119.72 (11)	S2—N1—C1	120.01 (15)
S1—N1—C1	120.03 (15)		
C2—C1—N1—S1	104.7 (2)	C2—C1—N1—S2	−69.6 (3)
C1—N1—S1—C11	−98.87 (18)	C1—N1—S2—C21	−94.31 (18)
N1—S1—C11—C12	−127.7 (2)	N1—S2—C21—C22	166.42 (19)
C11—C12—N12—O121	−68.9 (3)	C21—C22—N22—O221	27.3 (3)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C2—H2...O221 ⁱ	0.95	2.57	3.185 (3)	123
C13—H13...O21 ⁱⁱ	0.95	2.44	3.386 (3)	171
C14—H14...O22 ⁱⁱⁱ	0.95	2.46	3.336 (3)	153
C15—H15...O222 ⁱ	0.95	2.58	3.462 (3)	155
C23—H23...O22 ^{iv}	0.95	2.53	3.475 (3)	172
C26—H26...O11 ^v	0.95	2.50	3.230 (3)	134

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

Data collection: COLLECT (Nonius, 1997); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PRPKAPPA (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3028). Services for accessing these data are described at the back of the journal.

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