

N,N'-Propylenedioxybis(2,4,6-trimethylbenzenesulfonamide): molecules of unexpected conformation form a molecular ladder built from two independent N—H···O=S hydrogen bonds

Solange M. S. V. Wardell,^a Marcus V. D. Rangel e Silva,^a Patricia F. Prado,^a John N. Low^{b‡} and Christopher Glidewell^{c*}

^aDepartamento de Química Inorgânica, Instituto de Química, Universidade Federal Fluminense, 24020-150 Niterói, Rio de Janeiro, RJ, Brazil, ^bDepartment of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and ^cSchool of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland

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

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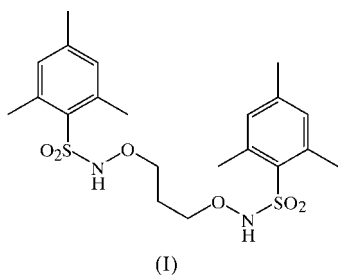
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Molecules of the title compound, C₂₁H₃₀N₂O₆S₂, adopt a skeletal conformation which does not possess even approximate internal symmetry. The molecules are linked by two N—H···O=S hydrogen bonds [H···O = 1.97 Å (×2), N···O = 2.865 (2) and 2.864 (2) Å, and N—H···O = 160 and 159°] into molecular ladders, alternatively described as chains of edge-fused R₂²(20) rings.

Comment

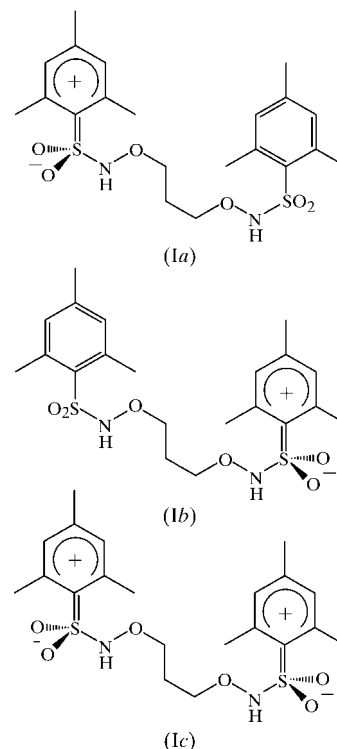
Terminally disubstituted bis[(2,4,6-trimethylbenzenesulfonyl)aminoxy]alkanes are useful intermediates for the synthesis of oxaza-macrocycles (Kuksa *et al.*, 1999), and we report here



the molecular and supramolecular structure of the title compound, (I), as a typical example of this class of intermediate.

[‡] Postal address: School of Engineering, University of Dundee, Dundee DD1 4HN, Scotland.

Molecules of (I) (Fig. 1) could, in principle, adopt a conformation having symmetry as high as C_{2v} ($mm2$); in the event, the molecules lie in general positions in space group $P\bar{1}$ ($Z' = 1$) and the molecular conformation precludes even approximate internal symmetry. Several of the corresponding pairs of torsion angles (Table 1) for the two halves of the molecule, from atom C2 to ring C11–C16 and from atom C2 to ring C21–C26, have similar values, but the conformations of



the non-H atoms about the O1—C1 and O2—C3 bonds are antiperiplanar and synclinal, respectively, while those around the C1—C2 and C3—C2 bonds are synclinal and antiperiplanar, respectively, so that the molecule as a whole has only C_1 symmetry (Fig. 1). Both of the S—N—O—C torsion angles appear to be determined by the mutual repulsion of the lone pairs of electrons on the N and O atoms, while each of the

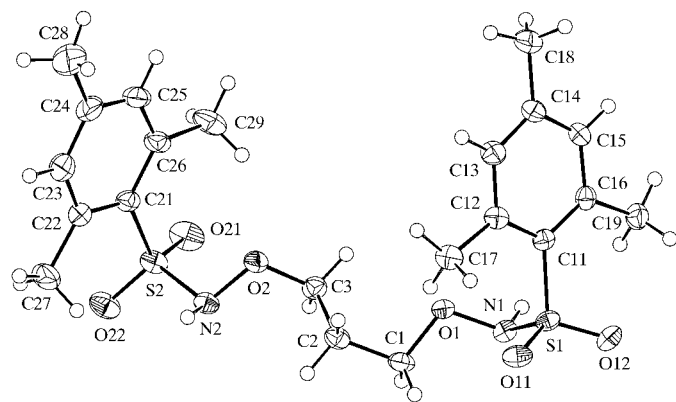


Figure 1

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

two aryl rings is approximately orthogonal to the adjacent CSN fragment. The conformational behaviour of the central fragment of the molecule between atoms S1 and S2 is unexpected and, at present, unexplained; given the orthogonality of the lone-pair orbitals on the adjacent N and O atoms, conformations having either C_s (m) or C_2 (2) symmetry might have been expected.

The bond lengths within the SO_2NOC fragments are typical of those observed in sulfonylhydroxylamines, such as $\text{PhSO}_2\text{-NHOH}$ and $\text{PhSO}_2\text{NHOSO}_2\text{Ph}$ (Scholz *et al.*, 1989). In the aryl rings, the $\text{C}n1\text{-C}n2$ and $\text{C}n1\text{-C}n6$ bonds ($n = 1$ or 2), adjacent to the sulfonyl substituents, have distances in the range 1.410 (2)–1.414 (2) Å, significantly longer than the other bonds in these rings, for which the distances lie in the range 1.382 (3)–1.399 (2) Å (mean 1.389 Å; Table 1). These values indicate some contribution to the overall molecular–electronic structure of charge-separated forms, such as (Ia)–(Ic).

Molecules of (I) are linked by pairs of inequivalent $\text{N}\cdots\text{H}\cdots\text{O}=\text{S}$ hydrogen bonds (Table 2). Amine atoms N1 and N2 in the molecule at (x, y, z) act as hydrogen-bond donors, respectively, to atom O11 in the molecule at $(-1+x, y, z)$ and to atom O21 in the molecule at $(1+x, y, z)$, so generating by translation a pair of independent and antiparallel $C(4)$ (Bernstein *et al.*, 1995) chains. This $C(4)$ motif is characteristic of the supramolecular aggregation in sulfonamides, sulfonylhydrazines and sulfonylhydroxylamines (Vorontsova, 1966;

Cotton & Stokeley, 1970; Klug, 1970; Brink & Mattes, 1986; Scholz *et al.*, 1989; Lightfoot *et al.*, 1993; Tremayne *et al.*, 1999, 2002).

The combination of the two $C(4)$ motifs generates a chain of edge-fused $R_2^2(20)$ (Bernstein *et al.*, 1995) rings running parallel to the [100] direction (Fig. 2). This chain may alternatively be regarded as a molecular ladder in which the two $C(4)$ chains provide the uprights and the sequence of atoms in the molecule running from N1 to N2 forms a rung of the ladder. This chain, or ladder, lies in the domain $-0.06 < z < 0.64$, and a second such ladder, related to the first by inversion, lies in the domain $0.36 < z < 1.06$. However, there are no direction-specific interactions between adjacent ladders. In particular, there are neither $\text{C}\cdots\text{H}\cdots\text{O}$ nor $\text{C}\cdots\text{H}\cdots\pi(\text{arene})$ hydrogen bonds and no aromatic $\pi\text{-}\pi$ stacking interactions; it seems probable that participation by the ring components in any of these interactions is precluded by the presence of the methyl substituents. The two shortest intermolecular $\text{H}\cdots\text{O}$ contacts both involve one the CH_2 groups in the central bridge, where the acidity of the $\text{C}\text{-H}$ bonds is expected to be low. Since both have $\text{H}\cdots\text{O}$ distances above 2.55 Å, *i.e.* not significantly less than the sum of the van der Waals radii, these contacts are not regarded as structurally significant.

Experimental

The title compound was prepared from 1,3-dibromopropane by means of successive reactions with (i) *N*-hydroxyphthalimide/dimethylformamide, (ii) HCl/acetic acid and (iii) 2,4,6-trimethylbenzenesulfonyl chloride/pyridine (Kuksa *et al.*, 1999). After recrystallization from toluene, the compound had a melting point of 433–435 K. Crystals suitable for single-crystal X-ray diffraction were selected directly from the recrystallized sample.

Crystal data

$\text{C}_{21}\text{H}_{30}\text{N}_2\text{O}_6\text{S}_2$
 $M_r = 470.59$
 Triclinic, $P\bar{1}$
 $a = 5.1689$ (1) Å
 $b = 14.3184$ (3) Å
 $c = 16.1506$ (4) Å
 $\alpha = 98.121$ (1)°
 $\beta = 97.963$ (1)°
 $\gamma = 99.033$ (1)°
 $V = 1152.75$ (4) Å³

$Z = 2$
 $D_x = 1.356$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5176 reflections
 $\theta = 3.4\text{--}27.5^\circ$
 $\mu = 0.27$ mm⁻¹
 $T = 120$ (2) K
 Plate, colourless
 $0.20 \times 0.10 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan (DENZO-SMN; Otwinowski & Minor, 1997)
 $T_{\min} = 0.954$, $T_{\max} = 0.989$
 17 653 measured reflections

5176 independent reflections
 4173 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.048$
 $\theta_{\max} = 27.5^\circ$
 $h = -6 \rightarrow 6$
 $k = -18 \rightarrow 18$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.108$
 $S = 1.02$
 5176 reflections
 286 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.3916P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.26$ e Å⁻³
 $\Delta\rho_{\min} = -0.48$ e Å⁻³

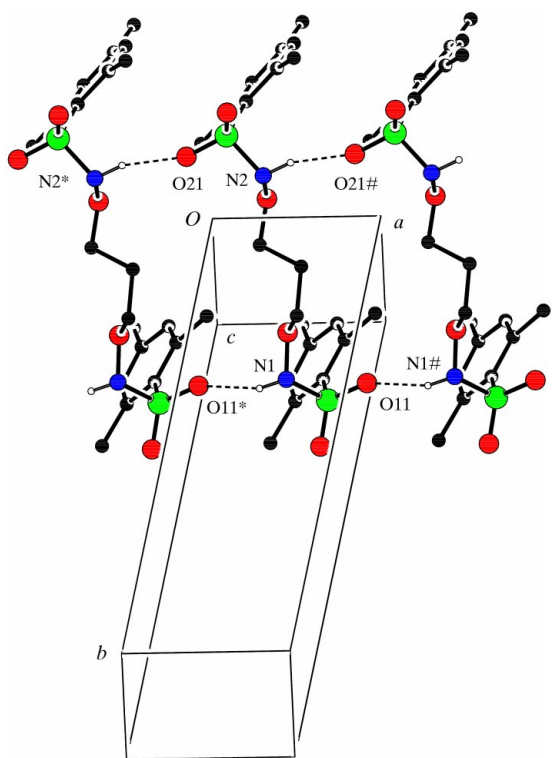


Figure 2

Part of the crystal structure of (I), showing the formation of a chain of edge-fused $R_2^2(20)$ rings along [100]. For clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(-1+x, y, z)$ and $(1+x, y, z)$, respectively.

Table 1

Selected geometric parameters (Å, °).

| | | | |
|---------------|--------------|---------------|--------------|
| S1—O11 | 1.4312 (12) | S2—O21 | 1.4307 (13) |
| S1—O12 | 1.4263 (13) | S2—O22 | 1.4266 (13) |
| S1—N1 | 1.6608 (14) | S2—N2 | 1.6653 (14) |
| S1—C11 | 1.7799 (16) | S2—C21 | 1.7747 (17) |
| O1—N1 | 1.4270 (17) | O2—N2 | 1.4284 (17) |
| O1—C1 | 1.4448 (19) | O2—C3 | 1.442 (2) |
| C11—C12 | 1.414 (2) | C21—C22 | 1.410 (2) |
| C11—C16 | 1.413 (2) | C21—C26 | 1.413 (2) |
| C12—C13 | 1.399 (2) | C22—C23 | 1.389 (3) |
| C13—C14 | 1.386 (2) | C23—C24 | 1.385 (3) |
| C14—C15 | 1.384 (3) | C24—C25 | 1.382 (3) |
| C15—C16 | 1.391 (2) | C25—C26 | 1.396 (3) |
| | | | |
| C12—C11—S1—N1 | 90.86 (13) | C22—C21—S2—N2 | −83.82 (14) |
| C11—S1—N1—O1 | −56.25 (11) | C21—S2—N2—O2 | −59.15 (11) |
| S1—N1—O1—C1 | −114.34 (11) | S2—N2—O2—C3 | −126.22 (11) |
| N1—O1—C1—C2 | 176.00 (12) | N2—O2—C3—C2 | −80.35 (16) |
| O1—C1—C2—C3 | 59.76 (18) | O2—C3—C2—C1 | −174.31 (13) |

Table 2

Hydrogen-bonding 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> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| N1—H1...O11 ⁱ | 0.94 | 1.97 | 2.865 (2) | 160 |
| N2—H2...O21 ⁱⁱ | 0.93 | 1.97 | 2.864 (2) | 159 |

Symmetry codes: (i) $x - 1, y, z$; (ii) $1 + x, y, z$.

Crystals of (I) are triclinic, and space group $P\bar{1}$ was selected and confirmed by the subsequent structure analysis. All H atoms were located from difference maps. H atoms bonded to C atoms were treated as riding atoms, with C—H distances of 0.95 (aromatic), 0.98 (CH₃) and 0.99 Å (CH₂). H atoms bonded to N atoms were allowed to ride at the positions identified from difference maps, giving N—H distances of 0.93 and 0.94 Å.

Data collection: *KappaCCD Server Software* (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*; 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: GG1212). Services for accessing these data are described at the back of the journal.

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