O21	0.3955 (2)	0.8576 (2)	0.5025 (1)	0.0892 (5)
O22	0.5640 (2)	0.6102 (2)	0.6759 (1)	0.0714 (6)
O23	0.5171 (2)	0.4774 (2)	0.7759 (1)	0.0664 (5)
O24	0.0894 (3)	0.8146 (3)	0.4658 (2)	0.1241 (8)
O25	0.2791 (2)	1.0039 (2)	0.6484 (1)	0.0528 (4)
O26	0.4637 (2)	1.0305 (2)	0.5795 (2)	0.0889 (6)
N21	0.2633 (2)	0.5843 (2)	0.5801 (2)	0.0519 (5)
N22	0.1231 (3)	0.5551 (2)	0.5586 (2)	0.0722 (8)
N23	0.0985 (3)	0.4877 (3)	0.6253 (2)	0.0762 (8)
C21	0.3578 (4)	0.9745 (3)	0.5145 (2)	0.0822 (9)
C22	0.2237 (3)	0.9722 (3)	0.5556 (2)	0.0600 (6)
C23	0.1799 (3)	0.8439 (3)	0.5504 (2)	0.0564 (6)
C24	0.3245 (3)	0.7867 (2)	0.5568 (2)	0.0467 (5)
C25	0.3188 (3)	0.6627 (3)	0.5200 (2)	0.0580 (6)
C26	0.2215 (3)	0.4731 (2)	0.6882 (2)	0.0584 (6)
C27	0.3290 (2)	0.5343 (2)	0.6613 (2)	0.0467 (5)
C28	0.4832 (2)	0.5466 (2)	0.7040 (2)	0.0490 (6)
C29	0.6671 (3)	0.4818 (4)	0.8265 (2)	0.083 (1)
C210	0.6817 (4)	0.3992 (6)	0.9038 (3)	0.119 (1)
C211	0.3629 (5)	1.2008 (4)	0.6356 (3)	0.104 (1)
C212	0.4030 (3)	1.0738 (3)	0.6519 (2)	0.0621 (8)
C213	0.5059 (4)	1.0528 (5)	0.7431 (3)	0.112 (1)

Table 2. *Selected geometric parameters (Å, °)*

O11—C11	1.406 (4)	O21—C21	1.404 (5)
O11—C14	1.435 (3)	O21—C24	1.417 (3)
O14—C13	1.414 (3)	O24—C23	1.402 (4)
N11—N12	1.338 (3)	N21—N22	1.340 (4)
N11—C15	1.471 (4)	N21—C25	1.447 (4)
N11—C17	1.355 (3)	N21—C27	1.360 (3)
N12—N13	1.312 (4)	N22—N23	1.320 (4)
N13—C16	1.343 (4)	N23—C26	1.337 (4)
C11—C12	1.540 (4)	C21—C22	1.532 (6)
C12—C13	1.519 (4)	C22—C23	1.521 (5)
C13—C14	1.524 (4)	C23—C24	1.505 (4)
C14—C15	1.517 (4)	C24—C25	1.516 (4)
C16—C17	1.370 (4)	C26—C27	1.369 (4)
C11—O11—C14	107.1 (2)	C21—O21—C24	107.8 (2)
N12—N11—C15	118.0 (2)	N22—N21—C25	119.0 (3)
N12—N11—C17	110.4 (2)	N22—N21—C27	110.1 (3)
C15—N11—C17	131.5 (2)	C25—N21—C27	130.9 (2)
N11—N12—N13	107.6 (2)	N21—N22—N23	107.2 (2)
N12—N13—C16	108.9 (2)	N22—N23—C26	109.3 (3)
O11—C11—C12	107.3 (2)	O21—C21—C22	107.0 (3)
C11—C12—C13	103.4 (2)	C21—C22—C23	103.8 (3)
O14—C13—C12	112.1 (2)	O24—C23—C22	112.4 (3)
O14—C13—C14	112.8 (2)	O24—C23—C24	108.7 (3)
C12—C13—C14	101.1 (2)	C22—C23—C24	100.4 (3)
O11—C14—C13	103.1 (2)	O21—C24—C23	104.9 (2)
O11—C14—C15	109.9 (2)	O21—C24—C25	108.2 (2)
C13—C14—C15	113.4 (2)	C23—C24—C25	115.1 (3)
N11—C15—C14	114.3 (2)	N21—C25—C24	110.1 (2)
N13—C16—C17	108.9 (3)	N23—C26—C27	108.8 (3)
N11—C17—C16	104.3 (2)	N21—C27—C26	104.5 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O14—H119$\cdots$N13^{i}	0.83 (6)	2.19 (6)	3.013 (3)	175 (5)
O24—H219$\cdots$N23^{ii}	0.84 (5)	1.99 (5)	2.806 (3)	165 (4)

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

All H atoms, except those attached to O atoms, were fixed at ideal positions (C—H distances set at 0.95 Å), with common isotropic displacement parameters fixed at $1.3B_{eq}$ of the atoms to which they are attached. From the systematic absences of $0k0$ and from subsequent least-squares refinement, the space group was determined to be $P2_1$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *MolEN*. Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1203). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Polymorph of Bis(2-nitrophenyl) Trisulfide

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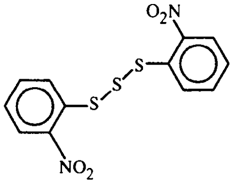
Abstract

Unlike the triclinic form, a molecular twofold axis in the orthorhombic form of bis(2-nitrophenyl) trisulfide, $C_{12}H_8N_2O_4S_3$, corresponds with the crystallographic symmetry.

Comment

A crystallographic study of the triclinic form of bis(2-nitrophenyl) trisulfide, (I), including details of its non-bonded S$\cdots$O interactions has been reported previously (Howie & Wardell, 1996).



(I)

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In the triclinic form, the molecular twofold axis is not related to the crystallographic symmetry. The present study of the orthorhombic form shows the molecular twofold axis passing through the central S2 atom, with symmetry-related atoms generated by the operation $(1-x,\ 1-y,\ z)$. This results in an angle of 67.8 (1)° between the normals of the best planes through the two aryl rings, whereas in the triclinic form, this angle is 113.1 (5)°. Short intermolecular S1···S2(x, y, $z-1$ and $1-x$, $1-y$, $z-1$) separations of 3.394 (2) Å are also present in the orthorhombic form, but no S···S separations less than the sum of the van der Waals radii (3.60 Å; Bondi, 1964) are reported for the triclinic form. There is also a small difference in the S—S—S angles [110.57 (9)° for orthorhombic and 106.35 (5)° for triclinic], but the remaining geometrical features are similar, for example, the intramolecular S···O separations are 2.585 (3) Å for the orthorhombic and 2.598 (3) and 2.592 (3) Å for the triclinic forms.

Each of the two molecules in the orthorhombic unit cell consists of two approximately linear sections, with an O1···S1—S2 angle of 173.75 (9)°. The S2···H3 intramolecular separation of 2.596 (4) Å is less than the sum of the corresponding van der Waals radii (3.00 Å; Bondi, 1964).

In the similar molecule diphenylsulfonyl sulfide, $PhSO_2SSO_2Ph$ (Mathieson & Robertson, 1949), molecular and crystallographic symmetry also coincide. Other polymorphic forms relevant to this study include the centrosymmetric and non-centrosymmetric forms of *m*-hydroxybenzoic acid (Gridunova *et al.*, 1982), plus polymorphs of other nitro compounds such as 3,5-dinitrobenzoic acid (Prince, Fronczek & Gandour, 1991) and 4′-nitrosalicylanilide (Etter, Urbanczyk-Lipkowska, Ameli & Panunto, 1988).

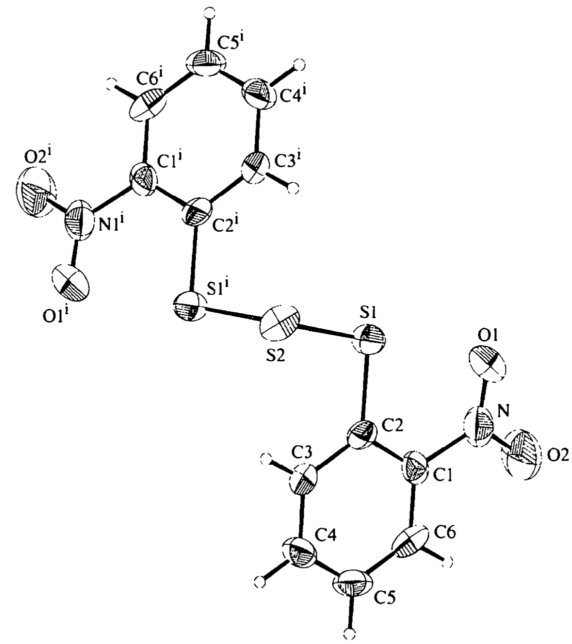

Fig. 1. The atomic arrangement in the molecule viewed approximately along the twofold axis passing through S2. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary radii. [Symmetry code: (i) $1-x$, $1-y$, z.]

Experimental

The orthorhombic form, isolated from a reaction mixture of PPh_3CCl, HSC_6H_4-*o*-NO_2 and Et_3N, was recrystallized from ethanol. HSC_6H_4-*o*-NO_2 was prepared from ClC_6H_4-*o*-NO_2 and NO_2S.

Crystal data

$C_{12}H_8N_2O_4S_3$
$M_r = 340.38$
Orthorhombic
$P2_12_12$
$a = 13.620$ (5) Å
$b = 12.088$ (5) Å
$c = 4.115$ (2) Å
$V = 677.5$ (5) Å^3
$Z = 2$
$D_x = 1.669$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 250 reflections
$\theta = 2.25$–24.96°
$\mu = 0.563$ mm^{-1}
$T = 150$ (2) K
Lozenge
0.32 × 0.28 × 0.16 mm
Orange

Data collection

Delft Instruments FAST diffractometer
Area-detector scans
Absorption correction: none
1960 measured reflections
1058 independent reflections

979 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0536$
$\theta_{\rm max} = 24.96°$
$h = 0 \rightarrow 14$
$k = -13 \rightarrow 13$
$l = -4 \rightarrow 4$

Refinement

Refinement on F^2
$R(F) = 0.0478$
$wR(F^2) = 0.1105$
$S = 1.089$
1058 reflections
100 parameters
H atoms refined in riding mode
$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.001$

$\Delta\rho_{\rm max} = 0.58$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.38$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = 0.40 (17)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S1	0.62235 (7)	0.47537 (8)	0.5825 (2)	0.0215 (3)
S2	1/2	1/2	0.8675 (3)	0.0244 (4)
O1	0.7861 (2)	0.4399 (2)	0.2828 (8)	0.0315 (8)
O2	0.8334 (2)	0.3042 (3)	−0.0190 (9)	0.0436 (10)
N	0.7744 (2)	0.3462 (3)	0.1698 (9)	0.0246 (8)
C1	0.6876 (3)	0.2846 (3)	0.2687 (10)	0.0184 (9)
C2	0.6144 (3)	0.3333 (3)	0.4565 (9)	0.0180 (9)
C3	0.5344 (3)	0.2670 (3)	0.5411 (10)	0.0209 (9)

C4	0.5297 (3)	0.1579 (3)	0.4410 (10)	0.0235 (10)
C5	0.6030 (3)	0.1121 (3)	0.2534 (10)	0.0241 (10)
C6	0.6817 (3)	0.1749 (3)	0.1667 (10)	0.0232 (10)

Table 2. *Selected geometric parameters (Å, °)*

S1—C2	1.798 (4)	O2—N	1.227 (5)
S1—S2	2.0595 (14)	N—C1	1.455 (5)
O1—N	1.235 (4)		
C2—S1—S2	104.69 (14)	C2—C1—N	121.4 (3)
S1^{i}—S2—S1	110.57 (9)	C6—C1—N	116.7 (3)
O2—N—O1	122.3 (3)	C1—C2—C3	117.1 (3)
O2—N—C1	119.8 (3)	C1—C2—S1	121.4 (3)
O1—N—C1	118.0 (3)	C3—C2—S1	121.6 (3)
C2—C1—C6	121.9 (3)		
C2—S1—S2—S1^{i}	−79.58 (12)	O1—N—C1—C6	−173.1 (3)
O2—N—C1—C2	−173.6 (3)	S2—S1—C2—C1	−177.3 (3)
O1—N—C1—C2	6.8 (5)	S2—S1—C2—C3	3.1 (4)
O2—N—C1—C6	6.5 (6)		

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

The unit cell was determined and the intensity data were collected on a Delft Instruments FAST diffractometer using the routines *ENDEX*, *REFINE* and *MADONL* in the *MADNES* software (Pflugrath & Messerschmidt, 1989), and processed using *ABSMAD* (Karaulov, 1992); detailed procedures are described by Darr, Drake, Hursthouse & Malik (1993). The S, O, N and C atoms were refined with anisotropic displacement parameters. The H atoms were allowed to ride on their attached C atoms and refined with isotropic displacement parameters.

Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1996).

The use of the EPSRC X-ray crystallographic service at the University of Wales, Cardiff, is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1114). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-(4-Bromophenyl)-2-fluoroethanone (2,4-Dinitrophenyl)hydrazone Containing a Particularly Short Fluorine–Hydrogen Bond

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Abstract

The title compound, 4-bromophenyl fluoromethyl ketone (2,4-dinitrophenyl)hydrazone, $C_{14}H_{10}BrFN_4O_4$, contains a short F···H contact [2.02 (3) Å] indicating an optimal stabilizing interaction.

Comment

We have a current interest (Howard, Hoy, O'Hagan & Smith, 1996) in exploring the ability of fluorine bound to carbon in organic compounds to act as a hydrogen-bond acceptor. Systematic analyses of the Cambridge Structural Database (Allen *et al.*, 1987; Howard *et al.*, 1996; Shimoni & Glusker, 1994; Murray-Rust, Stallings, Monti, Preston & Glusker, 1983) reveal very few situations where such F atoms form short F···H contacts to acidic H atoms and in general these interactions are overridden by stronger hydrogen-bonding interactions between OH and NH groups.

In attempts to design a system which may exhibit fluorine–hydrogen bonding, we have prepared the dinitrophenylhydrazone of 4-bromo-α-fluoroacetophenone, (I). The fluoromethyl group was selected following our calculations (Howard *et al.*, 1996), which suggest that fluorine attached to an sp^3 carbon will act as a better hydrogen-bond acceptor than fluorine attached to an sp^2 carbon. The title compound is shown to possess a particularly short F···H contact of 2.02 (3) Å to the hydrogen of the hydrazone group, as part of a three-centred interaction with an O atom of the *ortho*-nitro group. This length is close to the calculated equi-