organic compounds

2-(4-Nitrophenyl)-1,3-dithiane

Hoong-Kun Fun,[a]* Reza Kia,[a] Annada C. Maity[b] and Shyamaprosad Goswami[b]

[a]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah 711 103, India
Correspondence e-mail: hkfun@usm.my

The nitro group in the title compound, $C_{10}H_{11}NO_2S_2$, is almost coplanar with the benzene ring, making a dihedral angle of 3.42 (8)°. The 1,3-dithiane ring adopts a chair conformation. The crystal structure is stabilized by intermolecular C—H···O and C—H···π [C···Cg = 3.4972 (10) Å] interactions.

Related literature

For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For the calculation of ring puckering parameters, see: Cremer & Pople (1975). For related literature and applications see, for example: Goswami & Maity (2008); Fun *et al.* (2009).
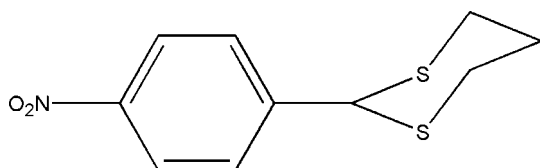
Experimental

Crystal data

$C_{10}H_{11}NO_2S_2$
$M_r = 241.32$
Orthorhombic, $P2_12_12_1$
$a = 8.7724$ (1) Å
$b = 10.2079$ (1) Å
$c = 11.9942$ (1) Å

$V = 1074.05$ (2) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.47$ mm^{-1}
$T = 100.0$ (1) K
$0.46 \times 0.22 \times 0.08$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.813$, $T_{max} = 0.964$

30643 measured reflections
4725 independent reflections
4511 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.061$
$S = 1.06$
4725 reflections
136 parameters
H-atom parameters constrained

$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
Absolute structure: Flack (1983), 2050 Friedel pairs
Flack parameter: 0.01 (4)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6A···O2^i	0.93	2.59	3.3346 (12)	137
C1—H1A···Cg1^{ii}	0.97	2.60	3.4972 (10)	154

Symmetry codes: (i) $-x + \frac{5}{2}, -y, z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, -y, z + \frac{1}{2}$. $Cg1$ is the centroid of the benzene ring.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2357).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555-1573.
Bruker (2005). *APEX2, SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Fun, H.-K., Kia, R., Maity, A. C. & Goswami, S. P. (2009). *Acta Cryst.* E**65**, o173.
Goswami, S. P. & Maity, A. C. (2008). *Tetrahedron Lett.* **49**, 3092–3096.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supporting information

2-(4-Nitrophenyl)-1,3-dithiane

Hoong-Kun Fun, Reza Kia, Annada C. Maity and Shyamaprosad Goswami

S1. Comment

Thioacetal protection of carbonyl groups is of paramount importance in synthetic organic chemistry and hence, the development of novel thionation reactions remains of great interest (Goswami & Maity, 2008; Fun *et al.,* 2009). In addition, thioacetals are also utilized as masked acyl anions or masked methylene functions in carbon-carbon bond forming reactions. Herein, we report the synthesis of 2-(4-nitro-phenyl)-[1,3]-dithiane (I) from 4-nitrobenzaldehyde using boron trifluoride etherate catalyst.

Compound (I), Fig. 1, comprises a single molecule in the asymmetric unit. The nitro group is almost coplanar with the benzene ring, making a dihedral angle of 3.42 (8)°. The thiacyclohexane ring adopts a chair conformation with the ring puckering parameters (Cremer & Pople, 1975) of $Q = 0.7137$ (8) Å, $\Theta = 173.96$ (7)°, and $\Phi = 135.6$ (7)°. The crystal structure is stabilized by intermolecular C—H···O and C—H···π interactions, Table 1.

S2. Experimental

To a stirred dichloromethane (50 mL) solution, maintained at 273 K, of 4-nitrobenzaldehyde (500 mg, 3.31 mmol) and boron trifluoride etherate (0.5 mL) was added dropwise 1,3-propanedithiol (450 mg, 4.1 mmol) over 15 min. The mixture was stirred at room temperature for 4 h and the progress of the reaction monitored by TLC. After completion of the reaction, $NaHCO_3$ solution was added carefully at room temperature to neutralize the mixture which was then extracted with dichloromethane. The organic layer was dried (anhydrous Na_2SO_4) and the solvent removed under reduced pressure. The crude product was purified by column chromatography using silica gel with 10% ethyl acetate in petroleum ether as eluant to afford (I) (674 mg, 84%) as a colourless crystalline solid along with the other thiane derivatives.

S3. Refinement

All hydrogen atoms were positioned geometrically and refined with a riding model approximation with C—H = 0.93-0.98 Å, and with U_{iso} (H) = 1.2 U_{eq} (C).
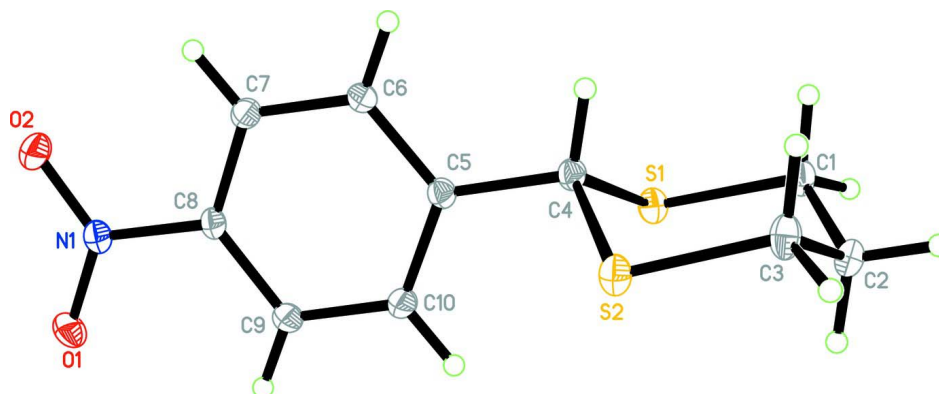
Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atomic numbering.

2-(4-Nitrophenyl)-1,3-dithiane

Crystal data

$C_{10}H_{11}NO_2S_2$	$F(000) = 504$
$M_r = 241.32$	$D_x = 1.492$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 9979 reflections
$a = 8.7724$ (1) Å	$\theta = 2.6$–38.5°
$b = 10.2079$ (1) Å	$\mu = 0.47$ mm^{-1}
$c = 11.9942$ (1) Å	$T = 100$ K
$V = 1074.05$ (2) Å^3	Block, colourless
$Z = 4$	$0.46 \times 0.22 \times 0.08$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	30643 measured reflections
Radiation source: fine-focus sealed tube	4725 independent reflections
Graphite monochromator	4511 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.038$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$\theta_{max} = 35.0°$, $\theta_{min} = 2.6°$
$T_{min} = 0.813$, $T_{max} = 0.964$	$h = -14 \rightarrow 14$
	$k = -16 \rightarrow 16$
	$l = -18 \rightarrow 19$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.024$	$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2 + 0.1305P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.061$	
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
4725 reflections	$\Delta\rho_{max} = 0.33$ e Å^{-3}
136 parameters	$\Delta\rho_{min} = -0.25$ e Å^{-3}
0 restraints	Absolute structure: Flack (1983), 2050 Friedel pairs
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: 0.01 (4)
Secondary atom site location: difference Fourier map	

Special details

Experimental. The low-temperature data was collected with the Oxford Cyrosystem Cobra low-temperature attachment.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	$U_{\text{iso}}*/U_{\text{eq}}$
S1	0.78978 (3)	0.06239 (2)	0.216265 (18)	0.01399 (5)
S2	1.07695 (3)	0.22170 (2)	0.261209 (18)	0.01492 (5)
O1	0.99728 (9)	0.26901 (8)	−0.32568 (6)	0.01819 (14)
O2	1.12536 (10)	0.08795 (8)	−0.33808 (6)	0.02137 (15)
N1	1.05536 (9)	0.17161 (8)	−0.28383 (7)	0.01391 (13)
C1	0.80248 (11)	0.03483 (9)	0.36543 (8)	0.01526 (16)
H1A	0.7009	0.0182	0.3941	0.018*
H1B	0.8631	−0.0431	0.3785	0.018*
C2	0.87227 (11)	0.14837 (10)	0.43022 (8)	0.01481 (15)
H2A	0.8157	0.2276	0.4135	0.018*
H2B	0.8618	0.1312	0.5094	0.018*
C3	1.03975 (11)	0.17104 (11)	0.40367 (8)	0.01636 (17)
H3A	1.0954	0.0907	0.4182	0.020*
H3B	1.0790	0.2376	0.4538	0.020*
C4	0.99151 (10)	0.08515 (9)	0.18616 (7)	0.01235 (15)
H4A	1.0463	0.0046	0.2055	0.015*
C5	1.01013 (10)	0.11049 (9)	0.06296 (7)	0.01189 (14)
C6	1.09657 (10)	0.02450 (9)	−0.00171 (7)	0.01299 (15)
H6A	1.1440	−0.0468	0.0318	0.016*
C7	1.11247 (10)	0.04450 (9)	−0.11583 (8)	0.01293 (15)
H7A	1.1690	−0.0131	−0.1593	0.016*
C8	1.04185 (10)	0.15252 (9)	−0.16301 (7)	0.01169 (14)
C9	0.95653 (11)	0.24152 (9)	−0.10131 (8)	0.01406 (16)
H9A	0.9114	0.3138	−0.1351	0.017*
C10	0.94071 (11)	0.21912 (9)	0.01268 (7)	0.01455 (15)
H10A	0.8836	0.2768	0.0558	0.017*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01279 (8)	0.01716 (10)	0.01201 (9)	−0.00234 (7)	−0.00105 (7)	−0.00003 (8)
S2	0.01512 (9)	0.01748 (10)	0.01216 (9)	−0.00450 (7)	0.00056 (7)	−0.00083 (7)
O1	0.0228 (3)	0.0179 (3)	0.0138 (3)	0.0016 (3)	−0.0017 (3)	0.0050 (3)
O2	0.0286 (4)	0.0219 (4)	0.0136 (3)	0.0056 (3)	0.0052 (3)	−0.0013 (3)
N1	0.0149 (3)	0.0152 (3)	0.0117 (3)	−0.0013 (3)	0.0008 (3)	0.0010 (3)

C1	0.0167 (4)	0.0169 (4)	0.0121 (4)	−0.0023 (3)	0.0021 (3)	0.0002 (3)
C2	0.0148 (4)	0.0183 (4)	0.0113 (4)	−0.0002 (3)	0.0016 (3)	−0.0019 (3)
C3	0.0147 (4)	0.0236 (4)	0.0108 (4)	−0.0019 (3)	−0.0012 (3)	−0.0010 (3)
C4	0.0133 (3)	0.0137 (4)	0.0100 (3)	0.0006 (3)	−0.0004 (3)	0.0001 (3)
C5	0.0127 (3)	0.0127 (3)	0.0103 (3)	0.0002 (3)	−0.0003 (3)	0.0006 (3)
C6	0.0142 (4)	0.0128 (3)	0.0120 (3)	0.0023 (3)	0.0001 (3)	0.0017 (3)
C7	0.0130 (3)	0.0134 (4)	0.0124 (3)	0.0009 (3)	0.0007 (3)	−0.0006 (3)
C8	0.0130 (3)	0.0131 (4)	0.0090 (3)	−0.0012 (3)	0.0005 (3)	0.0008 (3)
C9	0.0169 (4)	0.0130 (4)	0.0123 (4)	0.0025 (3)	0.0000 (3)	0.0015 (3)
C10	0.0182 (4)	0.0139 (4)	0.0116 (3)	0.0034 (3)	0.0007 (3)	0.0000 (3)

Geometric parameters (Å, º)

S1—C1	1.8145 (9)	C3—H3B	0.9700
S1—C4	1.8210 (9)	C4—C5	1.5090 (12)
S2—C3	1.8148 (10)	C4—H4A	0.9800
S2—C4	1.8208 (9)	C5—C6	1.3953 (13)
O1—N1	1.2248 (10)	C5—C10	1.4016 (13)
O2—N1	1.2368 (11)	C6—C7	1.3910 (13)
N1—C8	1.4670 (11)	C6—H6A	0.9300
C1—C2	1.5238 (13)	C7—C8	1.3855 (12)
C1—H1A	0.9700	C7—H7A	0.9300
C1—H1B	0.9700	C8—C9	1.3905 (13)
C2—C3	1.5210 (13)	C9—C10	1.3930 (13)
C2—H2A	0.9700	C9—H9A	0.9300
C2—H2B	0.9700	C10—H10A	0.9300
C3—H3A	0.9700		
C1—S1—C4	98.95 (4)	C5—C4—S1	108.74 (6)
C3—S2—C4	99.98 (4)	S2—C4—S1	113.56 (5)
O1—N1—O2	123.46 (8)	C5—C4—H4A	108.8
O1—N1—C8	118.63 (8)	S2—C4—H4A	108.8
O2—N1—C8	117.91 (8)	S1—C4—H4A	108.8
C2—C1—S1	114.18 (6)	C6—C5—C10	119.65 (8)
C2—C1—H1A	108.7	C6—C5—C4	119.69 (8)
S1—C1—H1A	108.7	C10—C5—C4	120.66 (8)
C2—C1—H1B	108.7	C7—C6—C5	120.61 (8)
S1—C1—H1B	108.7	C7—C6—H6A	119.7
H1A—C1—H1B	107.6	C5—C6—H6A	119.7
C3—C2—C1	113.39 (8)	C8—C7—C6	118.28 (8)
C3—C2—H2A	108.9	C8—C7—H7A	120.9
C1—C2—H2A	108.9	C6—C7—H7A	120.9
C3—C2—H2B	108.9	C7—C8—C9	122.91 (8)
C1—C2—H2B	108.9	C7—C8—N1	118.23 (8)
H2A—C2—H2B	107.7	C9—C8—N1	118.85 (8)
C2—C3—S2	114.47 (6)	C8—C9—C10	117.95 (8)
C2—C3—H3A	108.6	C8—C9—H9A	121.0
S2—C3—H3A	108.6	C10—C9—H9A	121.0

C2—C3—H3B	108.6	C9—C10—C5	120.59 (8)
S2—C3—H3B	108.6	C9—C10—H10A	119.7
H3A—C3—H3B	107.6	C5—C10—H10A	119.7
C5—C4—S2	107.96 (6)		
C4—S1—C1—C2	60.04 (8)	C4—C5—C6—C7	178.61 (8)
S1—C1—C2—C3	−66.54 (10)	C5—C6—C7—C8	0.73 (13)
C1—C2—C3—S2	64.81 (10)	C6—C7—C8—C9	0.18 (14)
C4—S2—C3—C2	−57.45 (8)	C6—C7—C8—N1	−178.43 (8)
C3—S2—C4—C5	179.49 (6)	O1—N1—C8—C7	−177.77 (8)
C3—S2—C4—S1	58.85 (6)	O2—N1—C8—C7	2.17 (12)
C1—S1—C4—C5	−179.95 (6)	O1—N1—C8—C9	3.56 (12)
C1—S1—C4—S2	−59.74 (6)	O2—N1—C8—C9	−176.50 (9)
S2—C4—C5—C6	117.37 (8)	C7—C8—C9—C10	−0.79 (14)
S1—C4—C5—C6	−119.01 (8)	N1—C8—C9—C10	177.81 (8)
S2—C4—C5—C10	−63.01 (10)	C8—C9—C10—C5	0.50 (14)
S1—C4—C5—C10	60.60 (10)	C6—C5—C10—C9	0.38 (14)
C10—C5—C6—C7	−1.01 (14)	C4—C5—C10—C9	−179.24 (9)

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C6—H6A⋯O2[i]	0.93	2.59	3.3346 (12)	137
C1—H1A⋯Cg1[ii]	0.97	2.60	3.4972 (10)	154

Symmetry codes: (i) −x+5/2, −y, z+1/2; (ii) −x+3/2, −y, z+1/2.