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S,S'-Butane-1,4-diyl bis(benzenecarbothioate)

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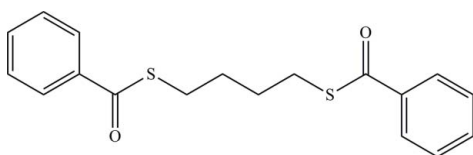
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.030; wR factor = 0.083; data-to-parameter ratio = 18.5.

The title compound, $\text{C}_{18}\text{H}_{18}\text{O}_2\text{S}_2$, which lies on an inversion center, adopts a *gauche*⁺–*trans*–*trans*–*trans*–*gauche*[−] (g^+tttg^-) conformation in the $\text{S}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}$ bond sequence. In the crystal, molecules are packed in a herringbone arrangement through intermolecular $\text{C}-\text{H}\cdots\pi$ interactions.

Related literature

For crystal structures and conformations of $\text{C}_6\text{H}_5\text{C}(=\text{O})\text{S}(\text{CH}_2)_n\text{SC}(=\text{O})\text{C}_6\text{H}_5$ ($n = 2, 3, 5, 7, 9$), see: for example, Deguire & Brisse (1988); Leblanc & Brisse (1992); Abe & Sasanuma (2012).



Experimental

Crystal data

$\text{C}_{18}\text{H}_{18}\text{O}_2\text{S}_2$
 $M_r = 330.44$
 Monoclinic, $P2_1/c$
 $a = 13.2230$ (14) Å
 $b = 4.8903$ (5) Å
 $c = 13.2638$ (15) Å
 $\beta = 106.897$ (1)°

$V = 820.67$ (15) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.33$ mm^{−1}
 $T = 173$ K
 $0.30 \times 0.30 \times 0.05$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{\min} = 0.908$, $T_{\max} = 0.984$

4326 measured reflections
 1845 independent reflections
 1626 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.083$
 $S = 1.05$
 1845 reflections

100 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.21$ e Å^{−3}
 $\Delta\rho_{\min} = -0.24$ e Å^{−3}

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C1–C6 phenyl ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C4}-\text{H4}\cdots\text{Cg1}^{\text{i}}$	0.95	3.09	3.8810 (15)	141

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008) and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS5305).

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supporting information

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S,S'*-Butane-1,4-diyl bis(benzenecarbothioate)*Daisuke Abe and Yuji Sasanuma****S1. Comment**

In expectation of superior properties such as chemical and thermal resistance, we have investigated structures and properties of polythioesters ($[-S(CH_2)_nSCOC_6H_4CO-]_x$, abbreviated as $PnTS_2$), where n denotes the number of methylene units. Instead of the polymer itself, a small model compound corresponding to the repeating unit is often employed to elucidate conformational characteristics of the polymer; therefore, we have adopted oligomethylenedithiobenzoate ($nDBS_2$). This paper describes synthesis and X-ray diffraction analysis of $4DBS_2$, a model compound of $P4TS_2$.

The crystal structure of $2DBS_2$ was determined previously (Deguire & Brisse, 1988). In the $2DBS_2$ crystal, the $S-CH_2-CH_2-S$ bonds lie in the *gauche*⁺ - *trans* - *gauche*⁻ (g^+tg^-) conformation. Our molecular orbital calculations and NMR experiments (Abe & Sasanuma, 2012) showed that this conformation is significantly stable even in isolated and liquid states owing to the anti-parallel arrangement of $S-C=O$ dipole moments (the intramolecular dipole-dipole interaction).

Figure 1 shows the molecular structure of $4DBS_2$. The $S-CH_2-CH_2-CH_2-CH_2-S$ part adopts the g^+ttg^- conformation, and the intramolecular dipole-dipole interaction similar to that of $2DBS_2$ may be formed; however, $2DBS_2$ and $4DBS_2$ have markedly different melting points and densities: 94 °C and 1.41 g cm⁻³ ($2DBS_2$); 49 °C and 1.34 g cm⁻³ ($4DBS_2$). These differences may be partly due to strengths of intermolecular interactions. In the $2DBS_2$ crystal, a number of intermolecular interactions such as $C=O\cdots H-C$, $C-H\cdots S$, and $C-H\cdots\pi$ can be found. In contrast, the $4DBS_2$ crystal has only a few $C-H\cdots\pi$ interactions (Fig. 2).

Crystal structures of $nDBS_2$ ($n = 3, 5, 7, 9$) were also reported (Leblanc & Brisse, 1992). The $nDBS_2$ molecules adopt (t) _{n} g^+ conformations in the $S-(CH_2)_n-S$ part. Interestingly, the $nDBS_2$ molecules show clear odd-even effects in the alkyl conformation: $g^+(t)_{n-1}g^-$ ($n = \text{even}$); (t) _{n} g^+ ($n = \text{odd}$).

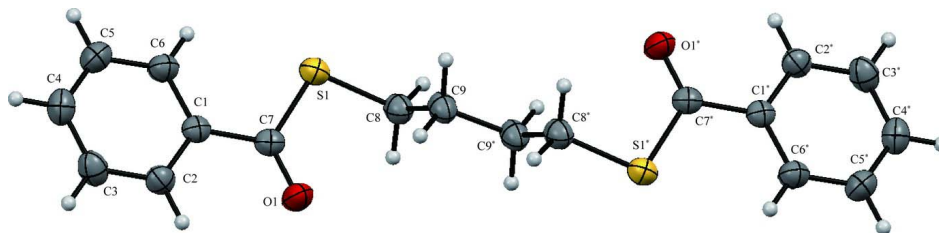
S2. Experimental

Benzoyl chloride (15.5 g, 0.11 mol) was added dropwise into 1,4-butanedithiol (6.1 g, 0.05 mol) and pyridine (8.7 g, 0.11 mol) kept at 0 °C, and then the mixture was stirred for 2 h. The crude product was diluted with diethyl ether (50 ml) and washed with water, 8% sodium hydrogen carbonate solution, and water. The organic layer was condensed, and white solid remained. The solid was recrystallized from ethanol to yield $4DBS_2$ (8.7 g, 53%).

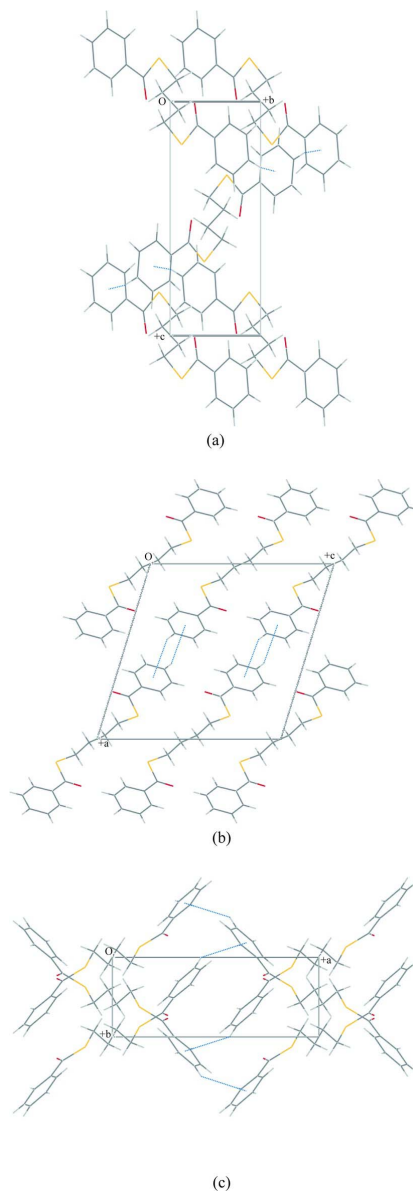
The product was dissolved in chloroform in an open vessel. The vessel was placed in a larger one containing methanol, a poor solvent for $4DBS_2$, to facilitate precipitation of crystals by vapor diffusion of methanol into the chloroform solution.

S3. Refinement

All C—H hydrogen atoms were geometrically positioned with C—H = 0.95 and 0.99 Å for the aromatic and methylene groups, respectively, and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

**Figure 1**

Molecular structure of *S,S'*-butane-1,4-diyl dibenzothioate (4DBS₂). Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

Packing diagram of 4DBS₂, viewed down the (a) a, (b) b, and (c) c axes. The dotted lines represent C—H... π interactions.

S,S'-Butane-1,4-diyl bis(benzenecarbothioate)*Crystal data*C₁₈H₁₈O₂S₂ $M_r = 330.44$ Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

 $a = 13.2230$ (14) Å $b = 4.8903$ (5) Å $c = 13.2638$ (15) Å $\beta = 106.897$ (1)° $V = 820.67$ (15) Å³ $Z = 2$ $F(000) = 348$ $D_x = 1.337$ Mg m⁻³

Melting point: 323 K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2016 reflections

 $\theta = 3.2$ – 26.8 ° $\mu = 0.33$ mm⁻¹ $T = 173$ K

Plate, colourless

 $0.30 \times 0.30 \times 0.05$ mm*Data collection*

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.333 pixels mm⁻¹ φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2001)

 $T_{\min} = 0.908$, $T_{\max} = 0.984$

4326 measured reflections

1845 independent reflections

1626 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.015$ $\theta_{\max} = 27.5$ °, $\theta_{\min} = 3.2$ ° $h = -15$ → 17 $k = -6$ → 6 $l = -13$ → 17 *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.030$ $wR(F^2) = 0.083$ $S = 1.05$

1845 reflections

100 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 0.1965P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.21$ e Å⁻³ $\Delta\rho_{\min} = -0.24$ e Å⁻³*Special details*

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.70285 (9)	0.4894 (3)	0.15671 (9)	0.0292 (3)
C2	0.62320 (10)	0.6555 (3)	0.09507 (10)	0.0350 (3)
H2	0.6032	0.6402	0.0205	0.042*

C3	0.57314 (11)	0.8429 (3)	0.14248 (12)	0.0422 (3)
H3	0.5188	0.9562	0.1003	0.051*
C4	0.60192 (12)	0.8656 (3)	0.25099 (12)	0.0414 (3)
H4	0.5688	0.9982	0.2832	0.050*
C5	0.67851 (12)	0.6964 (3)	0.31244 (11)	0.0427 (3)
H5	0.6968	0.7092	0.3870	0.051*
C6	0.72895 (11)	0.5077 (3)	0.26594 (10)	0.0376 (3)
H6	0.7814	0.3905	0.3087	0.045*
C7	0.75788 (10)	0.2993 (3)	0.10215 (10)	0.0311 (3)
C8	0.91038 (11)	-0.0700 (3)	0.08957 (11)	0.0377 (3)
H8A	0.9495	-0.2334	0.1244	0.045*
H8B	0.8470	-0.1342	0.0344	0.045*
C9	0.98021 (10)	0.0896 (3)	0.03740 (11)	0.0382 (3)
H9A	1.0415	0.1647	0.0924	0.046*
H9B	0.9397	0.2452	-0.0023	0.046*
O1	0.73074 (8)	0.2677 (2)	0.00745 (7)	0.0429 (3)
S1	0.86863 (3)	0.12549 (8)	0.18584 (3)	0.03886 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0297 (6)	0.0284 (6)	0.0294 (6)	-0.0041 (5)	0.0084 (5)	0.0010 (5)
C2	0.0353 (7)	0.0401 (7)	0.0308 (6)	0.0017 (5)	0.0115 (5)	0.0074 (5)
C3	0.0405 (7)	0.0437 (8)	0.0455 (8)	0.0097 (6)	0.0174 (6)	0.0129 (6)
C4	0.0428 (8)	0.0397 (7)	0.0477 (8)	0.0029 (6)	0.0224 (6)	-0.0016 (6)
C5	0.0469 (8)	0.0496 (9)	0.0322 (7)	0.0018 (7)	0.0123 (6)	-0.0050 (6)
C6	0.0392 (7)	0.0415 (8)	0.0294 (6)	0.0040 (6)	0.0057 (5)	0.0006 (6)
C7	0.0315 (6)	0.0308 (6)	0.0295 (6)	-0.0024 (5)	0.0063 (5)	0.0014 (5)
C8	0.0353 (7)	0.0341 (7)	0.0414 (7)	0.0042 (5)	0.0076 (6)	-0.0029 (6)
C9	0.0319 (7)	0.0347 (7)	0.0471 (8)	0.0018 (5)	0.0099 (6)	-0.0062 (6)
O1	0.0479 (6)	0.0495 (6)	0.0282 (5)	0.0103 (5)	0.0060 (4)	-0.0027 (4)
S1	0.0346 (2)	0.0456 (2)	0.0328 (2)	0.00686 (14)	0.00426 (14)	-0.00058 (14)

Geometric parameters (Å, °)

C1—C6	1.3913 (17)	C6—H6	0.9500
C1—C2	1.3916 (17)	C7—O1	1.2117 (15)
C1—C7	1.4912 (17)	C7—S1	1.7761 (13)
C2—C3	1.3841 (19)	C8—C9	1.5204 (19)
C2—H2	0.9500	C8—S1	1.8053 (14)
C3—C4	1.382 (2)	C8—H8A	0.9900
C3—H3	0.9500	C8—H8B	0.9900
C4—C5	1.377 (2)	C9—C9 ⁱ	1.526 (3)
C4—H4	0.9500	C9—H9A	0.9900
C5—C6	1.384 (2)	C9—H9B	0.9900
C5—H5	0.9500		
C6—C1—C2	119.39 (12)	C1—C6—H6	120.0

C6—C1—C7	122.48 (11)	O1—C7—C1	122.90 (12)
C2—C1—C7	118.13 (11)	O1—C7—S1	121.94 (10)
C3—C2—C1	119.98 (12)	C1—C7—S1	115.15 (9)
C3—C2—H2	120.0	C9—C8—S1	113.65 (10)
C1—C2—H2	120.0	C9—C8—H8A	108.8
C4—C3—C2	120.21 (13)	S1—C8—H8A	108.8
C4—C3—H3	119.9	C9—C8—H8B	108.8
C2—C3—H3	119.9	S1—C8—H8B	108.8
C5—C4—C3	120.04 (13)	H8A—C8—H8B	107.7
C5—C4—H4	120.0	C8—C9—C9 ⁱ	111.70 (14)
C3—C4—H4	120.0	C8—C9—H9A	109.3
C4—C5—C6	120.26 (13)	C9 ⁱ —C9—H9A	109.3
C4—C5—H5	119.9	C8—C9—H9B	109.3
C6—C5—H5	119.9	C9 ⁱ —C9—H9B	109.3
C5—C6—C1	120.06 (13)	H9A—C9—H9B	107.9
C5—C6—H6	120.0	C7—S1—C8	100.22 (6)
C6—C1—C2—C3	2.1 (2)	C6—C1—C7—O1	174.55 (14)
C7—C1—C2—C3	-177.31 (13)	C2—C1—C7—O1	-6.1 (2)
C1—C2—C3—C4	-0.1 (2)	C6—C1—C7—S1	-6.66 (18)
C2—C3—C4—C5	-1.8 (2)	C2—C1—C7—S1	172.72 (11)
C3—C4—C5—C6	1.7 (2)	S1—C8—C9—C9 ⁱ	175.95 (10)
C4—C5—C6—C1	0.4 (2)	O1—C7—S1—C8	-0.26 (14)
C2—C1—C6—C5	-2.3 (2)	C1—C7—S1—C8	-179.07 (11)
C7—C1—C6—C5	177.12 (14)	C9—C8—S1—C7	83.52 (11)

Symmetry code: (i) $-x+2, -y, -z$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

Cg1 is the centroid of the C1—C6 phenyl ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C4—H4 \cdots Cg1 ⁱⁱ	0.95	3.09	3.8810 (15)	141

Symmetry code: (ii) $-x+1, y+1/2, -z+1/2$.