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Butane-1,4-diyl bis(benzenecarbodithioate)

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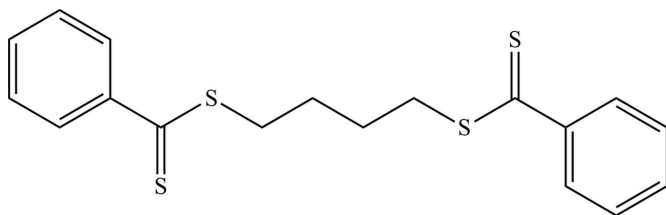
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.037; wR factor = 0.100; data-to-parameter ratio = 14.8.

The title compound, $\text{C}_{18}\text{H}_{18}\text{S}_4$, which lies on an inversion center, adopts a *trans-gauche*⁺–*trans-gauche*[–]–*trans* (*tg*⁺*tg*[–]*t*) conformation of the $\text{S}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}$ bond sequence. In the crystal, a $\pi-\pi$ interaction with a centroid-centroid distance of 3.8797 (16) Å is observed.

Related literature

For crystal structures and conformations of $\text{C}_6\text{H}_5\text{C}(=\text{S})\text{S}(\text{CH}_2)_2\text{SC}(=\text{S})\text{C}_6\text{H}_5$ and $\text{C}_6\text{H}_5\text{C}(=\text{O})\text{S}(\text{CH}_2)_4\text{SC}(=\text{O})\text{C}_6\text{H}_5$, see: Abe *et al.* (2011, 2013). For related compounds, see: Sawanobori *et al.* (2001); Sasanuma *et al.* (2002). For the synthesis of piperidinium dithiobenzoate, see: Kato *et al.* (1973).



Experimental

Crystal data

 $\text{C}_{18}\text{H}_{18}\text{S}_4$ $M_r = 362.56$

Monoclinic, $P2_1/n$
 $a = 11.0205$ (6) Å
 $b = 7.2535$ (5) Å
 $c = 11.3090$ (7) Å
 $\beta = 110.805$ (2)°
 $V = 845.06$ (9) Å³

$Z = 2$
 Cu $K\alpha$ radiation
 $\mu = 5.09$ mm^{–1}
 $T = 173$ K
 $0.40 \times 0.20 \times 0.01$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{\min} = 0.235$, $T_{\max} = 0.951$

4872 measured reflections
 1480 independent reflections
 1468 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.100$
 $S = 1.13$
 1480 reflections

100 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.35$ e Å^{–3}
 $\Delta\rho_{\min} = -0.31$ e Å^{–3}

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.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS5312).

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supporting information

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Butane-1,4-diyl bis(benzenecarbothioate)

Daisuke Abe and Yuji Sasanuma

S1. Comment

The aromatic polyesters, $[-O(CH_2)_nO(C=O)C_6H_4(C=O)-]_x$ ($n = 2-4$), have been mass-produced and used as fibers, films, bottles, and engineering plastics. In a series of our studies, we have investigated conformational characteristics and configurational properties of their analogs, $[-X(CH_2)_nX(C=Y)C_6H_4(C=Y)-]_x$, that is, polythioesters ($X = S, Y = O$, abbreviated herein as $PnTS_2$) and polydithioesters ($X = Y = S, PnTS_4$). As model compounds of $PnTS_2$ and $PnTS_4$, we have adopted oligomethylenedithiobenzoate ($nDBS_2$) and oligomethylenetetrathiobenzoate ($nDBS_4$), respectively. This paper describes synthesis and X-ray diffraction analysis of one of them, 4DBS₄.

Figure 1 shows the molecular structure of 4DBS₄. The S—CH₂—CH₂—CH₂—CH₂—S bonds lie in the *trans-gauche⁺-trans-gauche⁻-trans* (tg^+tg^-t) conformation. On the other hand, 4DBS₂, a model of P4TS₂, crystallizes to form the g^+ttg^- conformation (Abe & Sasanuma, 2013). In general, the S—CH₂ single bond prefers the *gauche* state (Sawanobori *et al.*, 2001; Sasanuma *et al.*, 2002). For instance, the crystalline 2DBS₄ molecule adopts the g^+tg^- conformation in the S—CH₂—CH₂—S linkage (Abe *et al.*, 2011). By contraries, the two S—CH₂ bonds of 4DBS₄ were found here to be in the *trans* conformation. Our molecular orbital calculations at the MP2/6-311+G(2 d,p)//B3LYP/6-311+G(2 d,p) level for gaseous 4DBS₄ yielded free energies (relative to the all-*trans* state) of the two conformers: 0.49 kcal mol⁻¹ (tg^+tg^-t) and -0.86 kcal mol⁻¹ (g^+ttg^-). Therefore, 4DBS₄ is not allowed to crystallize in the most stable conformation.

In differential scanning calorimetric measurements, a 4DBS₄ sample, which was recrystallized from methanol, exhibited only one endothermic peak at 68 °C on heating, whereas its melt-crystallized sample showed two endothermic peaks at 48 and 68 °C. The former and latter samples yielded powder X-ray diffraction patterns different from each other.

Interestingly, $nDBS_4$'s ($n = 2, 3, 4$, and 5) show odd-even effects in melting; 2DBS₄ and 4DBS₄, respectively, melt at 109 and 68 °C, whereas 3DBS₄ and 5DBS₄ are liquid at room temperature but exhibit glass transitions at -51 °C ($n = 3$) and -54 °C ($n = 5$).

S2. Experimental

Piperidinium dithiobenzoate (1.26 g, 5.3 mmol) was prepared according to the literature (Kato *et al.*, 1973). Dibromobutane (0.54 g, 2.5 mmol) was added dropwise into piperidinium dithiobenzoate dissolved in dimethylformamide (DMF, 15 ml) and then stirred for 8 h under nitrogen atmosphere. The reaction mixture was diluted with a mixture of ethyl acetate and n-hexane (1:4 in volume) and washed thrice with water, and the organic layer was dried overnight over anhydrous magnesium sulfate. The solution was condensed, dissolved in a toluene/n-hexane mixture (1:2 in volume), and fractionated by silica-gel chromatograph ($R_f = 0.3-0.5$). The collected fractions were condensed and recrystallized from a methanol/n-hexane mixture (1:1 in volume) to yield 4DBS₄ (0.37 g, 41%).

The product was dissolved in chloroform in an open vessel. The vessel was placed in a larger one containing n-hexane, a poor solvent for 4DBS₄, to facilitate precipitation of crystals by vapor diffusion of n-hexane 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 by $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

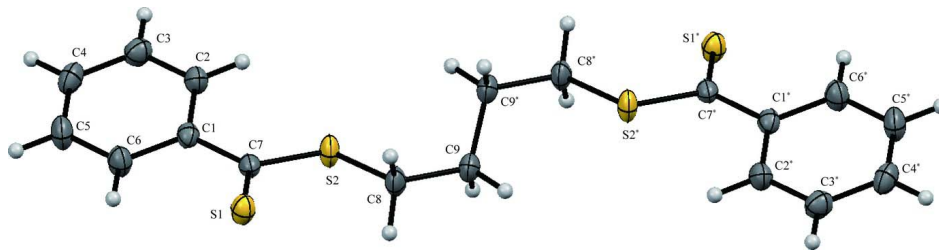


Figure 1

Molecular structure of *S,S'*-butane-1,4-diyl bis(benzenecarbodithioate) (4DBS₄). Displacement ellipsoids are drawn at the 50% probability level.

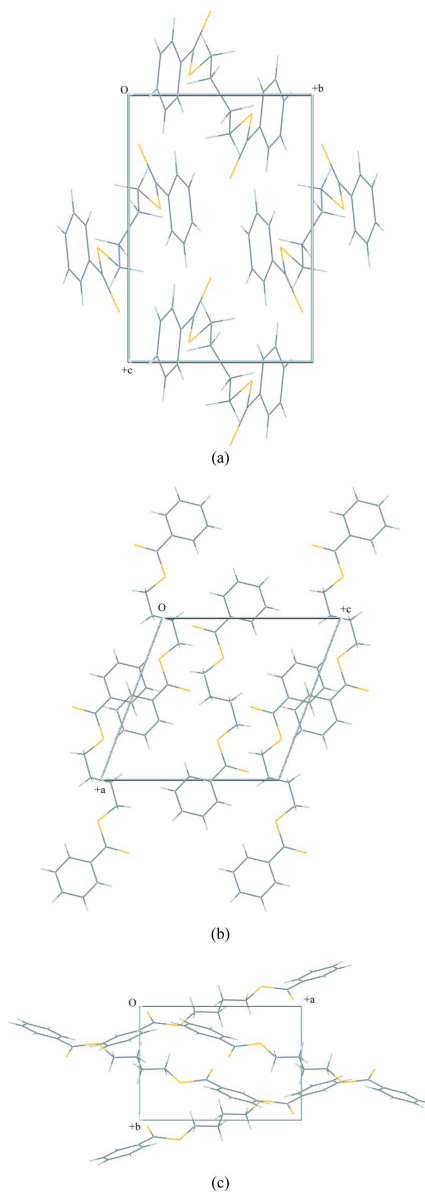


Figure 2

Packing diagrams of 4DBS₄, viewed down the *a* (a), *b* (b), and *c* (c) axes.

Butane-1,4-diyl bis(benzenecarbodithioate)

Crystal data

C₁₈H₁₈S₄

M_r = 362.56

Monoclinic, *P2₁/n*

Hall symbol: -*P* 2₁*n*

a = 11.0205 (6) Å

b = 7.2535 (5) Å

c = 11.3090 (7) Å

β = 110.805 (2)°

V = 845.06 (9) Å³

Z = 2

F(000) = 380

D_x = 1.425 Mg m⁻³

Melting point: 341 K

Cu *K*α radiation, λ = 1.54178 Å

Cell parameters from 5003 reflections

θ = 4.8–67.8°

μ = 5.09 mm⁻¹

T = 173 K

Plate, pink

0.40 × 0.20 × 0.01 mm

Data collection

Bruker APEXII CCD area-detector diffractometer	$T_{\min} = 0.235$, $T_{\max} = 0.951$
Radiation source: Bruker TXS fine-focus rotating anode	4872 measured reflections
Bruker Helios multilayer confocal mirror monochromator	1480 independent reflections
Detector resolution: 8.333 pixels mm ⁻¹	1468 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.028$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$\theta_{\max} = 68.1^\circ$, $\theta_{\min} = 4.8^\circ$
	$h = -13 \rightarrow 13$
	$k = -8 \rightarrow 7$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.037$	H-atom parameters constrained
$wR(F^2) = 0.100$	$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2 + 1.0478P]$
$S = 1.13$	where $P = (F_o^2 + 2F_c^2)/3$
1480 reflections	$(\Delta/\sigma)_{\max} < 0.001$
100 parameters	$\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	-0.0082 (2)	0.2157 (3)	0.3798 (2)	0.0226 (5)
C2	0.0225 (2)	0.2350 (4)	0.5097 (2)	0.0271 (5)
H2	0.1068	0.2029	0.5658	0.033*
C3	-0.0686 (2)	0.3004 (4)	0.5579 (2)	0.0309 (5)
H3	-0.0463	0.3138	0.6467	0.037*
C4	-0.1921 (2)	0.3461 (4)	0.4770 (3)	0.0314 (6)
H4	-0.2547	0.3904	0.5100	0.038*
C5	-0.2237 (2)	0.3270 (4)	0.3480 (3)	0.0347 (6)
H5	-0.3085	0.3581	0.2923	0.042*
C6	-0.1329 (2)	0.2628 (4)	0.2992 (2)	0.0300 (5)
H6	-0.1556	0.2508	0.2103	0.036*
C7	0.0885 (2)	0.1450 (3)	0.3270 (2)	0.0222 (5)
C8	0.3424 (2)	0.0498 (4)	0.3534 (2)	0.0288 (5)
H8A	0.3123	-0.0796	0.3375	0.035*
H8B	0.3313	0.1080	0.2710	0.035*

C9	0.4854 (2)	0.0543 (4)	0.4385 (2)	0.0270 (5)
H9A	0.5121	0.1841	0.4594	0.032*
H9B	0.5381	0.0031	0.3913	0.032*
S1	0.04887 (5)	0.05242 (9)	0.18505 (5)	0.0286 (2)
S2	0.24732 (5)	0.17228 (9)	0.42927 (5)	0.0278 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0177 (10)	0.0217 (12)	0.0276 (11)	−0.0011 (9)	0.0072 (9)	0.0005 (9)
C2	0.0197 (11)	0.0330 (13)	0.0271 (11)	0.0003 (10)	0.0064 (9)	0.0023 (10)
C3	0.0304 (12)	0.0364 (14)	0.0286 (12)	−0.0004 (11)	0.0136 (10)	−0.0013 (11)
C4	0.0255 (12)	0.0310 (14)	0.0429 (14)	0.0014 (10)	0.0186 (11)	−0.0034 (11)
C5	0.0189 (11)	0.0430 (16)	0.0389 (14)	0.0067 (11)	0.0063 (10)	−0.0015 (12)
C6	0.0210 (11)	0.0391 (15)	0.0269 (11)	0.0026 (10)	0.0047 (9)	−0.0026 (10)
C7	0.0169 (10)	0.0228 (12)	0.0255 (11)	0.0010 (8)	0.0058 (8)	0.0044 (9)
C8	0.0178 (11)	0.0406 (15)	0.0283 (11)	0.0071 (10)	0.0087 (9)	−0.0003 (10)
C9	0.0172 (11)	0.0335 (14)	0.0312 (12)	0.0040 (9)	0.0097 (9)	0.0022 (10)
S1	0.0211 (3)	0.0387 (4)	0.0246 (3)	−0.0006 (2)	0.0062 (2)	−0.0052 (2)
S2	0.0143 (3)	0.0394 (4)	0.0271 (3)	0.0035 (2)	0.0040 (2)	−0.0065 (2)

Geometric parameters (Å, °)

C1—C2	1.392 (3)	C6—H6	0.9500
C1—C6	1.395 (3)	C7—S1	1.649 (2)
C1—C7	1.487 (3)	C7—S2	1.732 (2)
C2—C3	1.386 (4)	C8—C9	1.527 (3)
C2—H2	0.9500	C8—S2	1.807 (2)
C3—C4	1.383 (4)	C8—H8A	0.9900
C3—H3	0.9500	C8—H8B	0.9900
C4—C5	1.381 (4)	C9—C9 ⁱ	1.530 (5)
C4—H4	0.9500	C9—H9A	0.9900
C5—C6	1.384 (3)	C9—H9B	0.9900
C5—H5	0.9500		
C2—C1—C6	118.6 (2)	C1—C6—H6	119.8
C2—C1—C7	121.2 (2)	C1—C7—S1	123.48 (16)
C6—C1—C7	120.2 (2)	C1—C7—S2	113.01 (16)
C3—C2—C1	120.7 (2)	S1—C7—S2	123.51 (13)
C3—C2—H2	119.6	C9—C8—S2	109.43 (16)
C1—C2—H2	119.6	C9—C8—H8A	109.8
C4—C3—C2	120.1 (2)	S2—C8—H8A	109.8
C4—C3—H3	120.0	C9—C8—H8B	109.8
C2—C3—H3	120.0	S2—C8—H8B	109.8
C5—C4—C3	119.6 (2)	H8A—C8—H8B	108.2
C5—C4—H4	120.2	C8—C9—C9 ⁱ	113.5 (2)
C3—C4—H4	120.2	C8—C9—H9A	108.9
C4—C5—C6	120.5 (2)	C9 ⁱ —C9—H9A	108.9

C4—C5—H5	119.7	C8—C9—H9B	108.9
C6—C5—H5	119.7	C9 ⁱ —C9—H9B	108.9
C5—C6—C1	120.4 (2)	H9A—C9—H9B	107.7
C5—C6—H6	119.8	C7—S2—C8	104.20 (11)
C6—C1—C2—C3	-0.3 (4)	C2—C1—C7—S1	158.30 (19)
C7—C1—C2—C3	-179.8 (2)	C6—C1—C7—S1	-21.2 (3)
C1—C2—C3—C4	0.5 (4)	C2—C1—C7—S2	-22.3 (3)
C2—C3—C4—C5	-0.3 (4)	C6—C1—C7—S2	158.2 (2)
C3—C4—C5—C6	-0.1 (4)	S2—C8—C9—C9 ⁱ	66.7 (3)
C4—C5—C6—C1	0.3 (4)	C1—C7—S2—C8	172.54 (17)
C2—C1—C6—C5	-0.1 (4)	S1—C7—S2—C8	-8.11 (19)
C7—C1—C6—C5	179.4 (2)	C9—C8—S2—C7	-176.88 (17)

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