Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Dibenzyl pentathiodicarbonate

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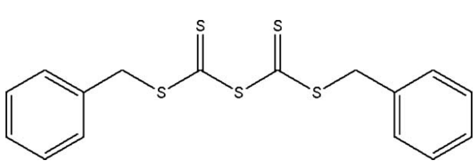
Received 9 November 2007; accepted 4 December 2007

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.006 Å; R factor = 0.061; wR factor = 0.107; data-to-parameter ratio = 20.4.

In the title compound, $C_{16}H_{14}S_5$, the non-bonded intramolecular distances between the non-terminal S atoms are 2.808 (16) and 2.784 (16) Å, shorter than the typical distance of 2.9 Å. One phenyl ring participates in an offset π-π interaction with another phenyl ring related by a centre of inversion; the interplanar distance is 3.41 (2) Å. The crystal structure also exhibits edge-to-face C—H$\cdots\pi$ stacking of the phenyl rings, thus forming a herring-bone packing motif.

Related literature

For related literature, see: Amin *et al.* (1979); Degani *et al.* (1986); McLeary & Klumperman (2006); Moad *et al.* (2005).



Experimental

Crystal data

$C_{16}H_{14}S_5$
M_r = 366.57
Monoclinic, $P2_1/n$
a = 8.4085 (18) Å
b = 19.670 (4) Å
c = 11.085 (3) Å
β = 111.953 (4)°
V = 1700.4 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.67 mm^{-1}
T = 100 (2) K
0.18 × 0.14 × 0.08 mm

Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: none
10376 measured reflections
3872 independent reflections
2278 reflections with $I > 2\sigma(I)$
R_{int} = 0.080

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.107
S = 0.92
3872 reflections
190 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C12—H12$\cdots Cg^{i}$	0.95	3.01	3.9056 (4)	163

Symmetry code: (i) $x+1, y, z+1$. Cg is the centroid of the ring C1–C6.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001; Atwood & Barbour, 2003); software used to prepare material for publication: *publCIF* (Westrip, 2008).

We thank Prof L. J. Barbour, Dr Martin Bredenkamp and Dr Catharine Esterhuysen for helpful discussions. Financial support for this work was provided by the National Research Foundation of South Africa. The data collection was undertaken on an instrument managed by the Central Analytical Facility at the University of Stellenbosch

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2221).

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supplementary materials

Acta Cryst. (2008). E**64**, o250 [**doi:10.1107/S1600536807065488**]

Dibenzyl pentathiodicarbonate

W. G. Weber, J. B. McLeary, J.-A. Gertenbach and L. Loots

Comment

Di- and trithiocarbonate systems have recently found widespread application as mediators in free radical polymerization (Moad *et al.*, 2005 and McLeary & Klumperman, 2006). As part of a further investigation of the interaction of these multithio compounds with radical species, extended polythiocarbonate systems have been examined. The preparation and characterization of pentathiodicarbonates is presented here. Two new dialkyl pentathiodicarbonates *R*–S–C(═S)–S–C(═S)–S–*R* with *R* = benzyl and *tert*-butyl were prepared by reaction of potassium benzyl- or *tert*-butyl-trithiocarbonate, respectively, with 2-chloro–*N*-methylpyridinium iodide (Scheme 2). The title compound is also formed by the reaction of potassium benzyltrithiocarbonate with benzyl dithiochloroformate (36% yield). The structure and details of the title compound are reported here.

The non-bonded intramolecular distance between S1 and S3 is 2.808 (16) Å and between S3 and S5 is 2.784 (16) Å. These are shorter than the 2.9 Å separation that is typically associated with distances of this type. The short contact is possible because of the out-of-plane twisting of the two thiono atoms, S2 and S4, and is likely brought about by steric hindrance between these two atoms. The intramolecular non-bonded distance between the two thiono atoms, S2 and S4, is 3.826 (16) Å.

The packing motif is mediated by the benzyl rings at either end of the molecule. For the purposes of this discussion we shall refer to the ring that is made up of C1, C2, C3, C4, C5 and C6 as Ring A and the ring consisting of C11, C12, C13, C14, C15 and C16 as Ring B. Ring A participates in an offset π-π interaction with another Ring A that is related by a centre of inversion. The linking methylene carbon atom (C7) also takes part in the interaction between these units. The interplanar spacing between the planes defined by the atoms of the two benzyl rings is 3.41 (2) Å. On its opposite side, Ring A interacts with a neighbouring Ring B, of a molecule related by *1 + x, y, 1 + z*, in an edge-to-face manner where H12 is situated 3.009 (4) Å from the plane defined by the atoms of Ring A.

Packing in the solid state is further mediated by a number of close contacts with neighbouring molecules, although none of the classical H-bond variety. A short intermolecular distance of 2.949 (4) Å is found between S5 and H5 of a molecule related by the *2 − x, −y, 1 − z* symmetry operation. S4 is separated from H14 (*x*, *y*, 1 + *z*) and S2 from H3 (*x-1,y, z − 1*) by 2.998 (4) Å and 3.048 (5) Å, respectively. S1 is at a distance of 3.011 Å (4) from H13 (*1 + x, y, 1 + z*).

Experimental

Potassium benzyltrithiocarbonate was prepared *in situ* by the reaction of benzyl mercaptan with carbon disulfide in aqueous potassium hydroxide (Degani,*et al.*, 1986) and 2-chloro-*N*-methylpyridinium iodide from 2-chloropyridine and methyl iodide (Amin *et al.*, 1979). Dibenzyl pentathiodicarbonate was prepared by adding 6.4 g (25 mmol) pyridinium salt within 5 min to a stirred and cooled aqueous solution of 50 mmol of potassium benzyl trithiocarbonate. Stirring continued for another 30 min and the red crystals formed were filtered off and washed several times with water. The crude product can be crystallized from acetonitrile with slow cooling to form larger red crystals. Yield = 7.6 g (83%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (p.p.m.):

7.30–7.35 (m, 10H, Ar), 4.52 (s, 4H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ (p.p.m.): 214.30 (C═S), 133.88, 129.51, 128.95 and 128.20 (C-aromatic), 43.00 (CH_2).

Refinement

H atoms were positioned geometrically and refined using a riding model [Csp^3—H = 0.99 Å and Csp^2—H = 0.95 Å; U_{iso}(H) = 1.2U_{eq}(C)].

Figures

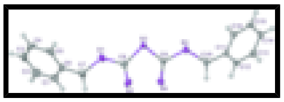

Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

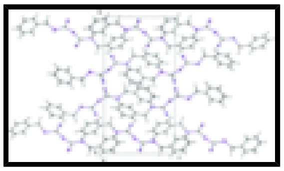

Fig. 2. The crystal packing of the title compound, viewed along [100], showing a herringbone packing motif.

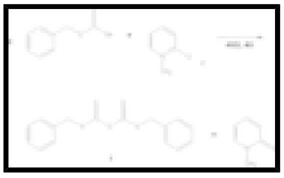

Fig. 3. The preparation of dibenzyl pentathiodicarbonate.

Dibenzyl pentathiodicarbonate

Crystal data

$C_{16}H_{14}S_5$	F_{000} = 760
M_r = 366.57	D_x = 1.432 Mg m^{-3}
Monoclinic, $P2_1/n$	Melting point: 318.15-319.15 K
Hall symbol: -P 2yn	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 8.4085 (18) Å	Cell parameters from 2278 reflections
b = 19.670 (4) Å	θ = 2.6–28.3°
c = 11.085 (3) Å	μ = 0.67 mm^{-1}
β = 111.953 (4)°	T = 100 (2) K
V = 1700.4 (6) Å^3	Block, red
Z = 4	0.18 × 0.14 × 0.08 mm

Data collection

Bruker APEX CCD area-detector diffractometer	2278 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.080
Monochromator: graphite	θ_{max} = 28.3°

T = 100(2) K	θ_{min} = 2.1°
ω scans	$h = -11 \rightarrow 6$
Absorption correction: none	$k = -24 \rightarrow 24$
10376 measured reflections	$l = -14 \rightarrow 14$
3872 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.061$	H-atom parameters constrained
$wR(F^2) = 0.107$	$w = 1/[\sigma^2(F_o^2) + (0.0279P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 0.92	$(\Delta/\sigma)_{max} < 0.001$
3872 reflections	$\Delta\rho_{max}$ = 0.47 e Å^{-3}
190 parameters	$\Delta\rho_{min}$ = −0.39 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2\sigma(F^2)$ 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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
S5	0.77686 (14)	0.15552 (5)	0.17633 (10)	0.0237 (3)
S1	1.03496 (15)	0.09626 (6)	0.69649 (11)	0.0306 (3)
S4	0.66740 (14)	0.21112 (5)	0.38636 (11)	0.0254 (3)
S3	0.96317 (13)	0.11315 (5)	0.42975 (11)	0.0255 (3)
S2	0.72043 (14)	0.02767 (5)	0.51002 (11)	0.0299 (3)
C11	0.6056 (5)	0.20472 (19)	−0.0574 (4)	0.0204 (9)
C10	0.6221 (5)	0.21790 (19)	0.0801 (4)	0.0224 (10)
H10A	0.5105	0.2118	0.0895	0.027*
H10B	0.6639	0.2647	0.1070	0.027*
C6	1.1089 (5)	0.05569 (19)	0.9414 (4)	0.0202 (9)
C13	0.4729 (5)	0.1434 (2)	−0.2583 (4)	0.0255 (10)
H13	0.3875	0.1128	−0.3104	0.031*
C14	0.5886 (5)	0.17070 (19)	−0.3055 (4)	0.0261 (10)

H14	0.5826	0.1594	−0.3904	0.031*
C8	0.8884 (5)	0.07591 (18)	0.5457 (4)	0.0231 (10)
C9	0.7847 (5)	0.16372 (18)	0.3323 (4)	0.0190 (9)
C16	0.7212 (5)	0.23211 (19)	−0.1066 (4)	0.0227 (10)
H16	0.8061	0.2632	−0.0553	0.027*
C5	1.2588 (6)	0.01676 (19)	0.9908 (5)	0.0278 (11)
H5	1.2793	−0.0183	0.9395	0.033*
C12	0.4803 (5)	0.1602 (2)	−0.1365 (4)	0.0243 (10)
H12	0.3991	0.1413	−0.1052	0.029*
C15	0.7139 (5)	0.2148 (2)	−0.2283 (4)	0.0265 (10)
H15	0.7954	0.2332	−0.2600	0.032*
C1	1.0855 (5)	0.1055 (2)	1.0204 (4)	0.0279 (11)
H1	0.9844	0.1324	0.9886	0.034*
C2	1.2013 (6)	0.1176 (2)	1.1416 (5)	0.0347 (12)
H2	1.1812	0.1527	1.1929	0.042*
C4	1.3762 (5)	0.0294 (2)	1.1135 (5)	0.0355 (12)
H4	1.4787	0.0034	1.1457	0.043*
C3	1.3486 (6)	0.0789 (2)	1.1907 (5)	0.0378 (13)
H3	1.4293	0.0864	1.2764	0.045*
C7	0.9785 (6)	0.0428 (2)	0.8083 (4)	0.0352 (12)
H7A	0.8623	0.0544	0.8049	0.042*
H7B	0.9796	−0.0057	0.7848	0.042*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S5	0.0273 (7)	0.0242 (6)	0.0186 (6)	0.0081 (5)	0.0073 (5)	0.0018 (5)
S1	0.0329 (7)	0.0374 (7)	0.0211 (7)	−0.0161 (6)	0.0097 (5)	−0.0005 (5)
S4	0.0272 (7)	0.0260 (6)	0.0265 (7)	0.0055 (5)	0.0142 (5)	0.0015 (5)
S3	0.0218 (6)	0.0297 (6)	0.0249 (6)	0.0061 (5)	0.0086 (5)	0.0076 (5)
S2	0.0257 (7)	0.0267 (6)	0.0302 (7)	−0.0055 (5)	0.0021 (5)	0.0040 (5)
C11	0.021 (2)	0.019 (2)	0.020 (2)	0.0088 (19)	0.0068 (19)	0.0058 (19)
C10	0.019 (2)	0.022 (2)	0.023 (3)	0.0065 (19)	0.0032 (19)	0.0024 (19)
C6	0.026 (3)	0.017 (2)	0.018 (2)	−0.0084 (19)	0.0096 (19)	−0.0011 (18)
C13	0.023 (3)	0.025 (2)	0.024 (3)	0.000 (2)	0.005 (2)	0.001 (2)
C14	0.035 (3)	0.026 (2)	0.018 (2)	0.007 (2)	0.010 (2)	0.0065 (19)
C8	0.026 (3)	0.019 (2)	0.024 (3)	0.0005 (19)	0.010 (2)	−0.0016 (19)
C9	0.016 (2)	0.019 (2)	0.021 (2)	−0.0035 (18)	0.0062 (18)	0.0039 (18)
C16	0.018 (2)	0.018 (2)	0.028 (3)	0.0034 (18)	0.004 (2)	0.0013 (19)
C5	0.040 (3)	0.014 (2)	0.043 (3)	−0.008 (2)	0.031 (3)	−0.006 (2)
C12	0.021 (2)	0.030 (3)	0.023 (3)	−0.002 (2)	0.010 (2)	0.002 (2)
C15	0.026 (3)	0.026 (2)	0.034 (3)	0.000 (2)	0.019 (2)	0.010 (2)
C1	0.027 (3)	0.021 (2)	0.036 (3)	0.006 (2)	0.013 (2)	0.002 (2)
C2	0.044 (3)	0.022 (3)	0.042 (3)	−0.006 (2)	0.020 (3)	−0.012 (2)
C4	0.014 (3)	0.036 (3)	0.055 (4)	0.006 (2)	0.011 (2)	0.024 (3)
C3	0.031 (3)	0.051 (3)	0.024 (3)	−0.022 (3)	0.002 (2)	0.007 (2)
C7	0.038 (3)	0.045 (3)	0.022 (3)	−0.019 (2)	0.011 (2)	0.002 (2)

Geometric parameters (Å, °)

S5—C9	1.713 (4)	C13—H13	0.9500
S5—C10	1.816 (4)	C14—C15	1.386 (5)
S1—C8	1.712 (4)	C14—H14	0.9500
S1—C7	1.818 (4)	C16—C15	1.371 (5)
S4—C9	1.626 (4)	C16—H16	0.9500
S3—C8	1.786 (4)	C5—C4	1.372 (6)
S3—C9	1.788 (4)	C5—H5	0.9500
S2—C8	1.623 (4)	C12—H12	0.9500
C11—C16	1.388 (5)	C15—H15	0.9500
C11—C12	1.398 (5)	C1—C2	1.353 (6)
C11—C10	1.500 (5)	C1—H1	0.9500
C10—H10A	0.9900	C2—C3	1.380 (6)
C10—H10B	0.9900	C2—H2	0.9500
C6—C1	1.375 (5)	C4—C3	1.371 (6)
C6—C5	1.400 (5)	C4—H4	0.9500
C6—C7	1.495 (5)	C3—H3	0.9500
C13—C12	1.368 (5)	C7—H7A	0.9900
C13—C14	1.374 (5)	C7—H7B	0.9900
C9—S5—C10	106.15 (18)	C11—C16—H16	119.7
C8—S1—C7	104.72 (19)	C4—C5—C6	119.8 (4)
C8—S3—C9	102.81 (18)	C4—C5—H5	120.1
C16—C11—C12	118.1 (4)	C6—C5—H5	120.1
C16—C11—C10	121.3 (4)	C13—C12—C11	121.0 (4)
C12—C11—C10	120.5 (4)	C13—C12—H12	119.5
C11—C10—S5	104.7 (2)	C11—C12—H12	119.5
C11—C10—H10A	110.8	C16—C15—C14	120.4 (4)
S5—C10—H10A	110.8	C16—C15—H15	119.8
C11—C10—H10B	110.8	C14—C15—H15	119.8
S5—C10—H10B	110.8	C2—C1—C6	122.4 (4)
H10A—C10—H10B	108.9	C2—C1—H1	118.8
C1—C6—C5	117.6 (4)	C6—C1—H1	118.8
C1—C6—C7	121.5 (4)	C1—C2—C3	120.1 (4)
C5—C6—C7	121.0 (4)	C1—C2—H2	120.0
C12—C13—C14	120.3 (4)	C3—C2—H2	120.0
C12—C13—H13	119.9	C3—C4—C5	121.4 (4)
C14—C13—H13	119.9	C3—C4—H4	119.3
C13—C14—C15	119.5 (4)	C5—C4—H4	119.3
C13—C14—H14	120.2	C4—C3—C2	118.7 (4)
C15—C14—H14	120.2	C4—C3—H3	120.6
S2—C8—S1	128.2 (2)	C2—C3—H3	120.6
S2—C8—S3	124.9 (3)	C6—C7—S1	107.0 (3)
S1—C8—S3	106.8 (2)	C6—C7—H7A	110.3
S4—C9—S5	128.8 (2)	S1—C7—H7A	110.3
S4—C9—S3	125.7 (2)	C6—C7—H7B	110.3
S5—C9—S3	105.34 (19)	S1—C7—H7B	110.3
C15—C16—C11	120.7 (4)	H7A—C7—H7B	108.6

C15—C16—H16	119.7		
C16—C11—C10—S5	−83.6 (4)	C7—C6—C5—C4	−179.8 (3)
C12—C11—C10—S5	91.5 (4)	C14—C13—C12—C11	−0.5 (6)
C9—S5—C10—C11	−174.6 (3)	C16—C11—C12—C13	0.7 (6)
C12—C13—C14—C15	0.7 (6)	C10—C11—C12—C13	−174.6 (4)
C7—S1—C8—S2	7.5 (3)	C11—C16—C15—C14	1.4 (6)
C7—S1—C8—S3	−168.2 (2)	C13—C14—C15—C16	−1.1 (6)
C9—S3—C8—S2	59.4 (3)	C5—C6—C1—C2	0.1 (6)
C9—S3—C8—S1	−124.7 (2)	C7—C6—C1—C2	179.5 (4)
C10—S5—C9—S4	5.7 (3)	C6—C1—C2—C3	−0.6 (7)
C10—S5—C9—S3	−170.05 (18)	C6—C5—C4—C3	1.3 (6)
C8—S3—C9—S4	42.3 (3)	C5—C4—C3—C2	−1.7 (6)
C8—S3—C9—S5	−141.73 (19)	C1—C2—C3—C4	1.4 (6)
C12—C11—C16—C15	−1.2 (6)	C1—C6—C7—S1	90.3 (4)
C10—C11—C16—C15	174.1 (3)	C5—C6—C7—S1	−90.4 (4)
C1—C6—C5—C4	−0.4 (6)	C8—S1—C7—C6	176.9 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12···Cg^{i}	0.95	3.01	3.9056 (4)	163

Symmetry codes: (i) x+1, y, z+1.

Fig. 1

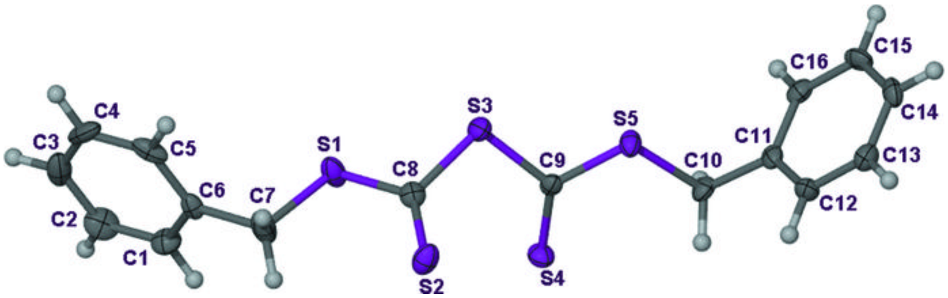

Fig. 2

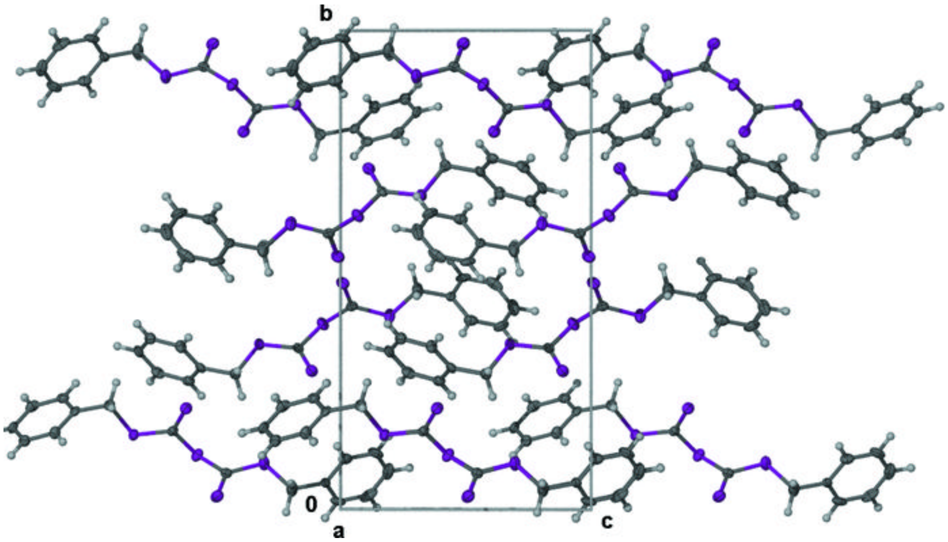

Fig. 3