Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Dibenzyl sulfide at 150 K

Christian Hansson

Organic Chemistry, Department of Chemistry, Lund University, PO Box 124, SE-221 00 Lund, Sweden

Correspondence e-mail: christian.hansson@organic.lu.se

Received 25 April 2006
Accepted 11 May 2006

Key indicators

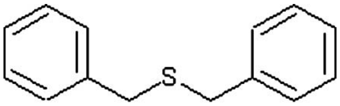
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.039
wR factor = 0.119
Data-to-parameter ratio = 29.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The molecule of the title compound, $C_{14}H_{14}S$, lies on a crystallographic twofold axis running through the central S atom, and hence molecules have exact C_2 molecular symmetry. Density-functional theory calculations reveal that the energy-optimized molecular structure in the gas phase is close to that observed in the crystal structure. The crystal packing is dominated by double chains running along the c axis formed by C—H···S interactions.

Comment

Apart from unit-cell parameters (Krc & French, 1953), full structural results have not previously been reported for dibenzyl sulfide (Bz_2S), (I), although a crystal structure of the 1:1 addition compound $Bz_2S\cdot I_2$ is known (Rømming, 1960).



(I)

An intensity data set was collected at 150 K, since the crystals sublimed at room temperature. The dibenzyl sulfide molecule (Fig. 1) lies on a crystallographic twofold axis running through the central S atom, and hence molecules have exact C_2 molecular symmetry. The S1—C1 and C1sp^3—C2sp^2 distances (Table 1), as well as C—C distances within the aromatic ring, are normal. The C—S—C angle is in the expected range for an sp^3-hybridized S atom. Besides the C_2 symmetry required by the crystallographic twofold axis, Bz_2S may adopt the molecular symmetries C_{2v}, C_s and C_1. Density-functional theory (DFT) calculations optimizing the geometry in the gas phase indicate that the observed conformation in the crystalline state is at a potential global minimum. Optimizations with C_s and C_{2v} conformations as starting geometries revealed three other minima with energies 2.3 (C_s), 5.8 (C_{2v}) and 6.4 (C_s) kJ mol^{-1} above the potential global minimum. The calculations thus indicate that the energetically favoured conformation is retained in the solid state.

Each dibenzyl sulfide molecule interacts with two neighbouring molecules, forming a double chain running in the c-axis direction (Fig. 2). The S atom accepts two interactions with *ortho*-H atoms in the two neighbouring molecules. The S1···H3^{ii} distance is 3.05 Å, the S1···H3^{ii}—C3^{ii} angle is 148°, and the C1—S1···H3^{ii} and C1—S1···H3^{iii} angles are 99 and 144°, respectively [symmetry codes: (ii) $1 - x, 1 - y, -z$; (iii) $1 + x, -y, -\frac{1}{2} + z$]. Mulliken charges obtained from DFT calculations on the observed conformation are −0.22 for sulfur and 0.08 for *ortho*-hydrogen. The formation of the

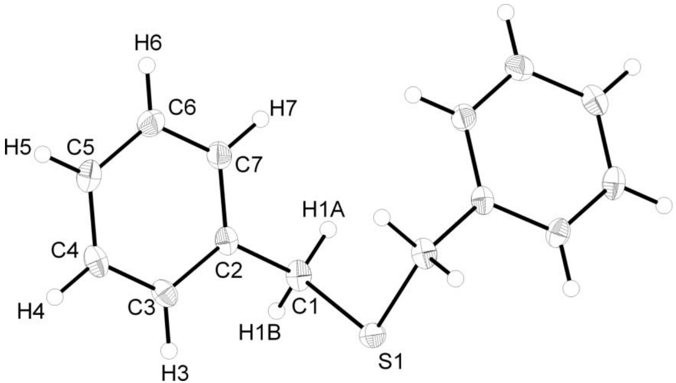


Figure 1
Molecular structure of (I), showing displacement ellipsoids drawn at the 30% probability level and H atoms as small spheres. Unlabelled atoms are related by the symmetry operator ($1 - x, y, \frac{1}{2} - x$).

double chain may thus be explained by S⋯H electrostatic interactions. A single-point DFT calculation on a pair of neighbouring molecules with two S⋯H interactions (Fig. 2) shows that such a formation gains an energy of 5.5 kJ mol^{-1} per two S⋯H interactions. The interactions between the double chains are mainly of the type C—H⋯π(arene), with a distance H4⋯$Cg^{\rm iv}$ = 2.747 (16) Å and C4—H4⋯$Cg1^{\rm iv}$ = 150.8 (14)°, where Cg is the centroid of the phenyl ring [symmetry code: (iv) $\frac{3}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$].

Experimental

Dibenzyl sulfide (98%) (CAS-no 538–74-9) was supplied from Aldrich Chemicals Co. and used without further purification or recrystallization. Quantum chemical geometry optimizations were performed with the density-functional theory (DFT) method at the B3LYP level as implemented in the *GAUSSIAN03* program package (Frisch *et al.*, 2003) with basis set STO-3G.

Crystal data

$C_{14}H_{14}S$
M_r = 214.31
Orthorhombic, *Pbcn*
a = 13.9913 (12) Å
b = 11.3985 (8) Å
c = 7.2081 (5) Å
V = 1149.55 (15) Å^3
Z = 4
D_x = 1.238 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 150 (1) K
Prism, colourless
0.22 × 0.20 × 0.16 mm

Data collection

Oxford Diffraction XCALIBUR3 diffractometer
ω scans
Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{\min}$ = 0.944, $T_{\max}$ = 0.969
10614 measured reflections
2020 independent reflections
1541 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.028
$\theta_{\max}$ = 32.8°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.119
S = 1.09
2020 reflections
69 parameters
All H-atom atomic coordinates refined
$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 0.1503P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.48 e Å^{-3}
$\Delta\rho_{\min}$ = −0.22 e Å^{-3}

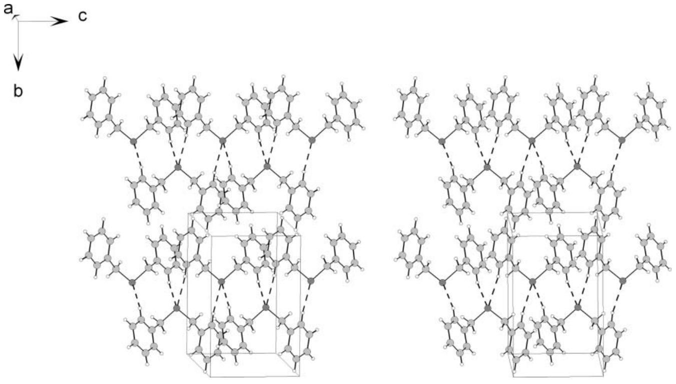


Figure 2
A stereoscopic partial packing plot of (I), showing C—H⋯S interactions as dashed lines.

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.8098 (12)	C7—C6	1.3898 (17)
C3—H3	0.963 (16)	C7—H7	0.992 (18)
C1—H1*B*	0.971 (15)	C5—C6	1.3859 (18)
C1—H1*A*	0.978 (17)	C5—H5	0.964 (19)
C4—H4	0.936 (18)	C6—H6	0.971 (19)
C1—S1—C1$^{\rm i}$	101.23 (8)	C2—C7—H7	119.1 (10)
C2—C1—S1	114.35 (7)	C6—C7—H7	119.8 (10)
S1—C1—H1*B*	110.6 (9)	C4—C5—C6	119.49 (11)
S1—C1—H1*A*	105.7 (10)	C4—C5—H5	119.7 (10)
C3—C4—C5	120.36 (11)	C6—C5—H5	120.9 (11)
C3—C4—H4	120.5 (12)	C5—C6—C7	120.02 (12)
C5—C4—H4	119.1 (12)	C5—C6—H6	119.5 (10)
C2—C7—C6	121.05 (10)	C7—C6—H6	120.5 (10)
C1$^{\rm i}$—S1—C1—C2	−72.49 (8)	S1—C1—C2—C3	−70.65 (12)
S1—C1—C2—C7	110.24 (11)	C1—C2—C7—C6	177.58 (10)

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

H-atom positions were refined isotropically as riding on their parent C atom, allowing the C—H distance to vary [0.936 (18)–0.992 (18) Å].

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *enCIFer* (Version 1.1; Allen *et al.*, 2004).

Professor Åke Oskarsson is thanked for valuable discussions. Financial assistance from the Royal Physiographic Society in Lund and the Wallenberg Foundation is acknowledged.

References

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.

Brandenburg, K. (2000). *DIAMOND*. Version 2.0. Crystal Impact, Bonn, Germany.

Frisch, M. J. *et al.* (2003). *GAUSSIAN03*. Revision A.6. Gaussian Inc., Pittsburgh, PA, USA.

Krc, J. & French, J. (1953). *Anal. Chem.* **25**, 198–199.

Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.29. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

Rømming, C. (1960). *Acta Chem. Scand.* **14**, 2145–2151.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97.* University of Göttingen, Germany.