organic compounds

Methylene bis(dithiobenzoate)

Yao-Ren Liang,[a] Hung-Chun Tong,[a] Yih-Hsing Lo,[a]* Chia-Her Lin[b] and Ting Shen Kuo[c]

[a]Department of Chemical Engineering, Tatung University, Taipei 104, Taiwan, [b]Department of Chemistry, Chung-Yuan Christian University, Chung-Li 320, Taiwan, and [c]Department of Chemistry, National Normal Taiwan University, Taipei 106, Taiwan

Correspondence e-mail: yhlo@ttu.edu.tw

In the title compound, $C_{15}H_{12}S_4$, two phenyldithiocarboxylate units are linked through a methylene C atom on a twofold rotation axis. The central $S-CH_2-S$ angle of 116.9 (5)° is significantly larger than the ideal tetrahedral value. The dihedral angle formed by the two phenyl rings is 68.2 (1)°. The refined Flack parameter of 0.2 (3) does not permit unambiguous determination of the absolute structure.

Related literature

For related structures, see: Shrivastav et al. (2002); Gonzalez-Castro et al. (2000); Quintanilla et al. (2005).
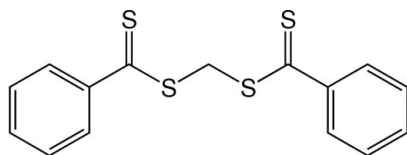
Experimental

Crystal data

$C_{15}H_{12}S_4$	$a = 11.5800$ (3) Å
$M_r = 320.49$	$b = 14.6440$ (11) Å
Orthorhombic, $P2_12_12$	$c = 4.2710$ (7) Å
$V = 724.27$ (13) Å³	$\mu = 0.64$ mm^{-1}
$Z = 2$	$T = 200$ (2) K
Mo $K\alpha$ radiation	$0.11 \times 0.08 \times 0.02$ mm

Data collection

Nonius KappaCCD diffractometer	5256 measured reflections
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	1317 independent reflections
$T_{min} = 0.933$, $T_{max} = 0.987$	931 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.096$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$	$\Delta\rho_{max} = 0.37$ e Å^{-3}
$wR(F^2) = 0.157$	$\Delta\rho_{min} = -0.46$ e Å^{-3}
$S = 1.13$	Absolute structure: Flack (1983),
1317 reflections	505 Friedel pairs
87 parameters	Flack parameter: 0.2 (3)
H-atom parameters constrained	

Data collection: COLLECT (Nonius, 1999); cell refinement: DENZO and SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BI2313).

References

Blessing, R. H. (1995). Acta Cryst. A**51**, 33–38.

Flack, H. D. (1983). Acta Cryst. A**39**, 876–881.

Gonzalez-Castro, A., Gutierrez-Perez, R., Penieres-Carrillo, G., Diaz-Torres, E., Toscano, R. A., Moya-Cabrera, M., Cabrera-Ortiz, C. & Alvarez-Toledano, C. (2000). Heteroatom. Chem. **11**, 120–128.

Nonius (1999). COLLECT. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Quintanilla, M. G., Guerra, E., Dotor, J., Maresova, J., Barba, F. & Martin, A. (2005). Phosphorus Sulfur Silicon Relat. Elem. **180**, 1691–1699.

Sheldrick, G. M. (2008). Acta Cryst. A**64**, 112–122.

Shrivastav, A., Singh, N. K. & Srivastava, G. (2002). Bioorg. Med. Chem. **10**, 2693–2704.

supplementary materials

Methylene bis(dithiobenzoate)

Y.-R. Liang, H.-C. Tong, Y.-H. Lo, C.-H. Lin and T. S. Kuo

Comment

During studies on the reactivity of the RuS_2 complex $\{Ru(Tp)(PPh_3)[S_2CC_6H_5]\}$, (hydridotripyrazol-1-ylborato-$\kappa^3N^2,N^{2'},N^{2''}$)(phenyldithiocarboxylato-κ^2S,S')(triphenylphosphine-κP)ruthenium, with CH_3CN in dichloromethane, we unexpectedly obtained crystals of the title compound. It consists of two phenyldithiocarboxylate units bridged by a methylene group. The ^{1}H NMR spectrum in $CDCl_3$ shows one singlet at 5.31 ppm, assignable to SCH_2S. The EI mass spectrum shows the molecular ion $[C_{15}H_{12}S_4]^+$ with the characteristic isotopic distribution patterns. In the crystal, the C2—S2 bond length of 1.643 (6) Å is slightly longer than expected for a C=S double bond (*ca* 1.61 Å), while the C2—S1 and C1—S1 distances of 1.743 (6) and 1.794 (5) Å, respectively, are clearly single bonds. The S—C—S angle of 116.9 (5)° is larger than the ideal tetrahedral value, probably due to repulsion between the CS_2 groups.

Experimental

The title compound was obtained unexpectedly during studies on the reactivity of $\{Ru(Tp)(PPh_3)[S_2CC_6H_5]\}$ with CH_3CN in dichloromethane. To a solution of $\{Ru(Tp)(PPh_3)[S_2CC_6H_5]\}$ (2.00 g, 2.73 mmol) in CH_2Cl_2 (20 ml), an excess of CH_3CN (2 ml) was added. The resulting yellow solution was heated to reflux for 3 h and the yellow precipitate obtained was filtered and washed with methanol and water to remove excess reagents. The compound was then dried under vacuum to give 0.83 g (91% yield). Crystals for X-ray structure analysis were obtained by recrystallization of the crude product from dichloromethane–hexane.

Elemental analysis calculated: C, 56.21; H, 3.77%; found: C, 56.19; H, 3.69%. ^{1}H NMR ($CDCl_3$, 303 K, ppm): δ 7.98–7.35 (m, 10H, Ph), 5.31 (s, 2H, CH_2). MS (*m/z*): 320.5 (M^+).

Refinement

H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.95–0.96 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The refined Flack parameter of 0.2 (3) does not permit unambiguous determination of the absolute structure.
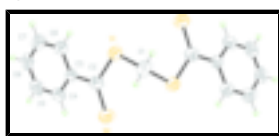
Figures

Fig. 1. Molecular structure of the title compound showing displacement ellipsoids at the 50% probability level for non-H atoms. Non-labelled atoms are related to labelled atoms by the symmetry code 1-*x*, 2-*y*, *z*.

supplementary materials

Methylene bis(dithiobenzoate)

Crystal data

$C_{15}H_{12}S_4$	$F_{000} = 332$
$M_r = 320.49$	$D_x = 1.470$ Mg m^{-3}
Orthorhombic, $P2_12_12$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: P 2 2ab	Cell parameters from 5256 reflections
$a = 11.5800$ (3) Å	$\theta = 2.0–25.4°$
$b = 14.6440$ (11) Å	$\mu = 0.64$ mm^{-1}
$c = 4.2710$ (7) Å	$T = 200$ (2) K
$V = 724.27$ (13) Å^3	Plate, yellow
$Z = 2$	$0.11 \times 0.08 \times 0.02$ mm

Data collection

Nonius KappaCCD diffractometer	1317 independent reflections
Radiation source: fine-focus sealed tube	931 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.096$
$T = 200(2)$ K	$\theta_{max} = 25.5°$
φ scans	$\theta_{min} = 2.2°$
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	$h = -13 \rightarrow 13$
$T_{min} = 0.933$, $T_{max} = 0.987$	$k = -17 \rightarrow 17$
5256 measured reflections	$l = -5 \rightarrow 4$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.056$	$w = 1/[\sigma^2(F_o^2) + (0.0733P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.157$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.13$	$\Delta\rho_{max} = 0.37$ e Å^{-3}
1317 reflections	$\Delta\rho_{min} = -0.46$ e Å^{-3}
87 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 505 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.2 (3)

Special details

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 $F^2 > \sigma(F^2)$ 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	$U_{iso}*/U_{eq}$
S1	0.47264 (14)	0.89784 (9)	0.5726 (3)	0.0446 (5)
S2	0.72612 (15)	0.92562 (10)	0.5091 (5)	0.0613 (6)
C1	0.5000	1.0000	0.792 (2)	0.049 (2)
H1A	0.4346	1.0109	0.9253	0.058*
C2	0.6098 (5)	0.8635 (4)	0.4525 (14)	0.0437 (15)
C3	0.6104 (5)	0.7734 (4)	0.2900 (15)	0.0381 (14)
C4	0.7071 (5)	0.7447 (4)	0.1238 (15)	0.0480 (17)
H4A	0.7733	0.7828	0.1147	0.058*
C5	0.7082 (6)	0.6617 (4)	−0.0279 (16)	0.0572 (18)
H5A	0.7749	0.6428	−0.1397	0.069*
C6	0.6127 (6)	0.6064 (4)	−0.0173 (15)	0.0562 (18)
H6A	0.6136	0.5491	−0.1211	0.067*
C7	0.5161 (6)	0.6336 (4)	0.1422 (16)	0.0600 (19)
H7A	0.4503	0.5949	0.1492	0.072*
C8	0.5140 (6)	0.7159 (4)	0.2913 (15)	0.0499 (17)
H8A	0.4459	0.7345	0.3977	0.060*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0456 (9)	0.0410 (8)	0.0472 (9)	−0.0042 (7)	0.0029 (7)	0.0005 (7)
S2	0.0472 (10)	0.0568 (9)	0.0800 (14)	−0.0132 (7)	−0.0145 (9)	0.0109 (10)
C1	0.063 (7)	0.043 (5)	0.039 (5)	−0.008 (4)	0.000	0.000
C2	0.042 (4)	0.048 (3)	0.041 (3)	−0.003 (2)	−0.012 (3)	0.017 (3)
C3	0.035 (3)	0.035 (3)	0.044 (4)	0.001 (3)	0.000 (3)	0.016 (3)
C4	0.038 (4)	0.058 (4)	0.048 (4)	0.002 (3)	0.002 (3)	0.018 (3)
C5	0.055 (4)	0.062 (4)	0.054 (4)	0.019 (3)	0.016 (4)	0.011 (4)
C6	0.068 (5)	0.039 (3)	0.062 (4)	0.013 (3)	0.012 (4)	−0.001 (4)
C7	0.057 (5)	0.046 (3)	0.077 (5)	−0.001 (3)	0.017 (4)	−0.005 (3)
C8	0.044 (4)	0.042 (3)	0.064 (4)	0.003 (3)	0.008 (4)	0.001 (3)

Geometric parameters ($Å$, °)

S1—C2	1.743 (6)	C4—H4A	0.950
S1—C1	1.794 (5)	C5—C6	1.370 (9)
S2—C2	1.643 (6)	C5—H5A	0.950
C1—S1[i]	1.794 (5)	C6—C7	1.369 (8)

C1—H1A	0.960	C6—H6A	0.950
C2—C3	1.491 (8)	C7—C8	1.364 (8)
C3—C4	1.391 (8)	C7—H7A	0.950
C3—C8	1.399 (8)	C8—H8A	0.950
C4—C5	1.377 (9)		
C2—S1—C1	103.5 (2)	C6—C5—C4	119.9 (6)
S1—C1—S1^i	116.9 (5)	C6—C5—H5A	120.1
S1—C1—H1A	108.0	C4—C5—H5A	120.1
S1^i—C1—H1A	108.0	C7—C6—C5	120.3 (6)
C3—C2—S2	123.6 (4)	C7—C6—H6A	119.9
C3—C2—S1	113.4 (4)	C5—C6—H6A	119.9
S2—C2—S1	123.0 (4)	C8—C7—C6	120.2 (7)
C4—C3—C8	117.5 (6)	C8—C7—H7A	119.9
C4—C3—C2	120.6 (5)	C6—C7—H7A	119.9
C8—C3—C2	121.8 (5)	C7—C8—C3	121.1 (6)
C5—C4—C3	121.0 (6)	C7—C8—H8A	119.5
C5—C4—H4A	119.5	C3—C8—H8A	119.5
C3—C4—H4A	119.5		
C2—S1—C1—S1^i	78.0 (2)	C2—C3—C4—C5	−179.7 (5)
C1—S1—C2—C3	174.1 (4)	C3—C4—C5—C6	0.3 (9)
C1—S1—C2—S2	−6.7 (5)	C4—C5—C6—C7	0.3 (10)
S2—C2—C3—C4	−12.4 (8)	C5—C6—C7—C8	0.2 (10)
S1—C2—C3—C4	166.7 (5)	C6—C7—C8—C3	−1.3 (10)
S2—C2—C3—C8	169.3 (5)	C4—C3—C8—C7	1.8 (9)
S1—C2—C3—C8	−11.6 (7)	C2—C3—C8—C7	−179.8 (6)
C8—C3—C4—C5	−1.4 (9)		

Symmetry codes: (i) −x+1, −y+2, z.

Fig. 1