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N′-[Bis(methylsulfanyl)methylidene]-2-methoxybenzohydrazide

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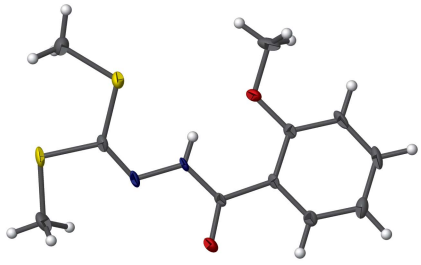
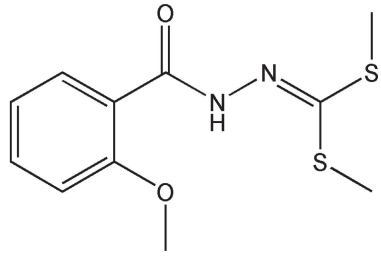
In the title compound, $C_{11}H_{14}N_2O_2S_2$, the diethyl dithioate groups are inclined slightly to the benzoyl ring, making a dihedral angle of 14.0 (3)°. A short intramolecular N—H···O contact generates an *S*(6) ring. In the crystal, C—H···O contacts generate a *C*(8) chain motif along [010].

3D view



Chemical scheme



Structure description

Dithiocarbazates and their *S*-alkyl/aryl esters containing nitrogen–sulfur donor atoms have shown interesting biological properties (Bharti *et al.*, 2000). Some dimethyl benzoylcarbonohydrazonodithioates exhibit activity against *Mycobacterium tuberculosis* (Gobis *et al.*, 2011). The *S*-alkyl/aryl esters exhibit efficient capacity for coordination with metals to form complexes (Ali *et al.*, 2008; Singh *et al.*, 2010, 2012). The *S*-alkyl/aryl esters derived from potassium salts of *N*-aroylhydrazinecarbodithioates have been found to be more stable towards cyclization compared to potassium *N*-aroylhydrazinecarbodithioates and form stable complexes with transition metal ions (Singh *et al.*, 2009; Bharty *et al.*, 2012).

In the title compound, the sum of the bond angles around C9 (360°) and the S1—C9—S2 bond angle of 117.39 (11)° clearly indicate sp^2 behavior similar to other reported bis-alkyl dithioesters (Nath *et al.*, 2015; Gobis *et al.*, 2011). The dihedral angle between the bis-methylsulfanylmethylidene group and the benzoyl ring is 14.0 (3)°. The C8—N1 and C9—N2 bond lengths [1.347 (2) and 1.285 (3) Å, respectively] are intermediate between typical C—N and C═N bond lengths, suggesting delocalization of the π electron density over the C8/N1/N2/C9 linkage (Jasinski *et al.*, 2010). In addition, an intramolecular N—H···O hydrogen bond is observed (Fig. 1 and Table 1).

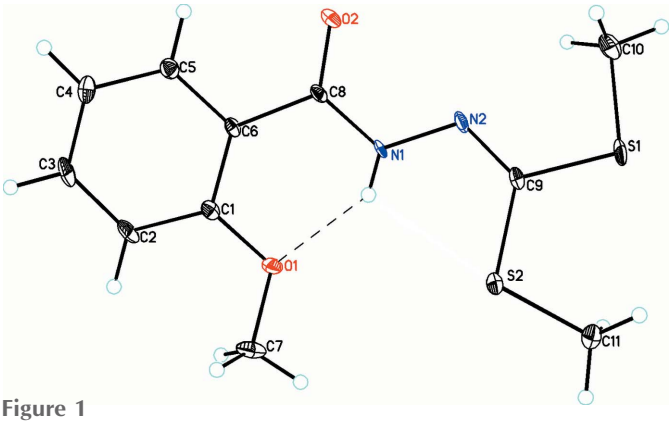


Figure 1
The molecular structure of title compound, $C_{11}H_{14}N_2O_2S_2$ with displacement ellipsoids drawn at the 30% probability level.

The crystal packing features intermolecular C—H···O hydrogen bonds between H atoms of the bis-methylsulfanylmethylidene group and the O atom of the benzoyl group, forming zigzag chains along the *b* axis direction (Table 1, Fig. 2).

Synthesis and crystallization

The title compound was synthesized by the dropwise addition of methyl iodide (20.0 mmol, 1.30 ml) to a suspension of potassium (2-methoxybenzoyl)hydrazinecarbodithioate (10.0 mmol, 2.38 g) in ethanol (20 ml) and stirring the reaction mixture for a period of 3–4 h. The resulting solution was acidified with dilute CH_3COOH (20% *v*/*v*), which yielded a white precipitate. This was washed with water and dried in *vacuo*. Colorless crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution over a period of 7 d (Fig. 3). (Yield 65%; m.p. 400–402 K). Analysis calculated for $C_{11}H_{14}N_2O_2S_2$ (%): C, 48.87; H, 5.20; N, 10.36; S, 23.71. Found: C, 49.12; H, 5.35; N, 10.22; S, 23.44. IR (selected, KBr): 3261 [ν(N—H)], 1654 [ν(C═O)], 1078 [ν(N—N)], 756 [ν(C—S)] cm^{-1}. ^1H NMR (DMSO-d_6); δ (p.p.m.) = 11.19 (*s*, 1H, NH), 7.96–7.01 (*m*, 4H,

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···O1	0.78 (3)	1.97 (3)	2.627 (2)	141 (2)
C10—H10*A*···O2^{i}	0.98	2.37	3.326 (3)	166
C11—H11*A*···O2^{ii}	0.98	2.61	3.341 (3)	131

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{14}N_2O_2S_2$
M_r	270.36
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	173
a, *b*, *c* (Å)	7.7829 (3), 7.4284 (3), 21.9087 (7)
β (°)	94.399 (3)
V (Å^3)	1262.91 (8)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	3.77
Crystal size (mm)	0.50 × 0.47 × 0.15
Data collection	
Diffractometer	Agilent Xcalibur, Eos, Gemini
Absorption correction	Multi-scan (SCALE3 ABSPACK in *CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.290, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4470, 2367, 2189
R_{int}	0.039
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.615
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.125, 1.08
No. of reflections	2367
No. of parameters	162
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.37, −0.33

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014/7* (Sheldrick, 2015*b*) and *SHELXTL* (Sheldrick, 2008).

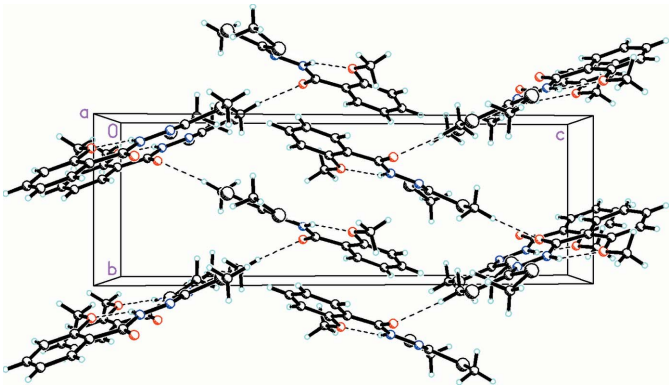


Figure 2
The packing of title compound, $C_{11}H_{14}N_2O_2S_2$ viewed along the *a* axis. Dashed lines indicate intramolecular N—H···O and intermolecular C—H···O hydrogen bonds.

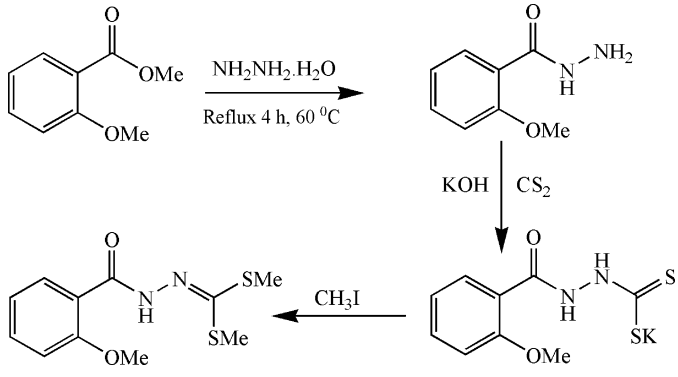


Figure 3
Reaction scheme showing the synthesis of the title compound, $C_{11}H_{14}N_2O_2S_2$.

C_6H_4, phenyl), 3.96 (*s*, 3H, –OCH_3), 2.43 (*s*, 6H, –CH_3). ^{13}C NMR (DMSO-d_6); δ (p.p.m.) = 165.3 (C9), 160.3 (C8), 157.6 (C1), 134.2 (C3), 131.8 (C5), 121.8 (C4), 121.0 (C6), 112.6 (C2), 56.8 (C7), 17.7–15.5 (C10, C11).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

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Crystal data

$C_{11}H_{14}N_2O_2S_2$
M_r = 270.36
Monoclinic, $P2_1/n$
a = 7.7829 (3) Å
b = 7.4284 (3) Å
c = 21.9087 (7) Å
β = 94.399 (3)°
V = 1262.91 (8) Å^3
Z = 4
$F(000)$ = 568
D_x = 1.422 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 2383 reflections
θ = 6.7–71.3°
μ = 3.77 mm^{-1}
T = 173 K
Thick plate, colorless
0.50 × 0.47 × 0.15 mm

Data collection

Agilent Xcalibur, Eos, Gemini diffractometer
Radiation source: fine-focus sealed X-ray tube
Detector resolution: 16.0416 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (SCALE3 ABSPACK in CrysAlisPro; Rigaku OD, 2015)
T_{min} = 0.290, T_{max} = 1.000
4470 measured reflections
2367 independent reflections
2189 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 71.4°, θ_{min} = 4.1°
h = −9→7
k = −8→8
l = −26→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.125
S = 1.08
2367 reflections
162 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0789P)^2 + 0.3498P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}
Extinction correction: *SHELXL2014/7* (Sheldrick 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0078 (13)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.56603 (7)	0.46135 (8)	0.25046 (2)	0.0268 (2)
S2	0.78152 (6)	0.59368 (8)	0.36113 (2)	0.0251 (2)
O1	0.63724 (17)	0.6970 (2)	0.51244 (6)	0.0216 (3)
O2	0.17729 (18)	0.7559 (2)	0.40453 (6)	0.0264 (4)
N1	0.4544 (2)	0.6643 (2)	0.40715 (7)	0.0154 (4)
H1N	0.539 (3)	0.652 (3)	0.4280 (12)	0.023 (6)*
N2	0.4351 (2)	0.5994 (2)	0.34749 (7)	0.0176 (4)
C1	0.4993 (2)	0.7762 (3)	0.53693 (8)	0.0147 (4)
C2	0.5060 (3)	0.8398 (3)	0.59679 (8)	0.0223 (5)
H2A	0.6093	0.8281	0.6225	0.027*
C3	0.3628 (3)	0.9202 (3)	0.61912 (9)	0.0266 (5)
H3A	0.3692	0.9649	0.6599	0.032*
C4	0.2108 (3)	0.9360 (3)	0.58261 (10)	0.0250 (5)
H4A	0.1123	0.9903	0.5979	0.030*
C5	0.2049 (3)	0.8710 (3)	0.52332 (9)	0.0177 (4)
H5A	0.1000	0.8809	0.4983	0.021*
C6	0.3460 (2)	0.7921 (2)	0.49882 (8)	0.0127 (4)
C7	0.7980 (3)	0.6926 (3)	0.54850 (11)	0.0292 (5)
H7A	0.8859	0.6375	0.5247	0.044*
H7B	0.7856	0.6216	0.5856	0.044*
H7C	0.8329	0.8156	0.5599	0.044*
C8	0.3180 (2)	0.7356 (3)	0.43279 (8)	0.0139 (4)
C9	0.5758 (3)	0.5576 (3)	0.32388 (8)	0.0170 (4)
C10	0.3382 (3)	0.4499 (4)	0.23262 (11)	0.0396 (6)
H10A	0.3141	0.3849	0.1940	0.059*
H10B	0.2911	0.5721	0.2286	0.059*
H10C	0.2846	0.3865	0.2655	0.059*
C11	0.9276 (3)	0.4888 (3)	0.31271 (10)	0.0295 (5)
H11A	1.0464	0.5108	0.3291	0.044*
H11B	0.9104	0.5393	0.2714	0.044*
H11C	0.9057	0.3588	0.3111	0.044*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0328 (3)	0.0384 (4)	0.0097 (3)	−0.0020 (2)	0.0038 (2)	−0.01010 (19)
S2	0.0212 (3)	0.0391 (4)	0.0151 (3)	−0.0011 (2)	0.0019 (2)	−0.0105 (2)
O1	0.0139 (7)	0.0363 (8)	0.0139 (7)	0.0024 (6)	−0.0031 (5)	0.0007 (6)
O2	0.0198 (7)	0.0460 (10)	0.0123 (7)	0.0050 (7)	−0.0051 (5)	−0.0039 (6)
N1	0.0165 (8)	0.0251 (9)	0.0042 (7)	0.0005 (7)	−0.0025 (6)	−0.0027 (6)
N2	0.0224 (8)	0.0240 (9)	0.0061 (7)	−0.0018 (7)	−0.0007 (6)	−0.0024 (6)
C1	0.0175 (9)	0.0174 (9)	0.0093 (8)	−0.0038 (7)	0.0008 (7)	0.0041 (7)
C2	0.0279 (11)	0.0293 (11)	0.0087 (9)	−0.0072 (9)	−0.0056 (7)	0.0024 (8)
C3	0.0404 (13)	0.0306 (11)	0.0090 (9)	−0.0068 (9)	0.0024 (8)	−0.0052 (8)
C4	0.0316 (12)	0.0270 (11)	0.0174 (10)	0.0010 (9)	0.0096 (9)	−0.0043 (8)

C5	0.0191 (9)	0.0203 (9)	0.0138 (9)	−0.0011 (7)	0.0013 (7)	0.0004 (7)
C6	0.0177 (9)	0.0139 (8)	0.0064 (8)	−0.0024 (7)	0.0006 (6)	0.0030 (6)
C7	0.0166 (10)	0.0377 (13)	0.0317 (12)	−0.0021 (9)	−0.0093 (8)	0.0064 (10)
C8	0.0157 (9)	0.0190 (9)	0.0068 (8)	−0.0019 (7)	−0.0013 (6)	0.0027 (7)
C9	0.0234 (10)	0.0193 (9)	0.0084 (8)	−0.0014 (7)	0.0013 (7)	−0.0004 (7)
C10	0.0357 (14)	0.0588 (17)	0.0227 (11)	0.0033 (12)	−0.0086 (10)	−0.0190 (11)
C11	0.0262 (11)	0.0416 (13)	0.0210 (11)	0.0064 (10)	0.0047 (9)	−0.0059 (10)

Geometric parameters (Å, º)

S1—C9	1.7564 (19)	C3—H3A	0.9500
S1—C10	1.788 (3)	C4—C5	1.383 (3)
S2—C9	1.761 (2)	C4—H4A	0.9500
S2—C11	1.792 (2)	C5—C6	1.389 (3)
O1—C1	1.369 (2)	C5—H5A	0.9500
O1—C7	1.428 (2)	C6—C8	1.506 (2)
O2—C8	1.225 (2)	C7—H7A	0.9800
N1—C8	1.347 (2)	C7—H7B	0.9800
N1—N2	1.391 (2)	C7—H7C	0.9800
N1—H1N	0.78 (3)	C10—H10A	0.9800
N2—C9	1.285 (3)	C10—H10B	0.9800
C1—C2	1.391 (3)	C10—H10C	0.9800
C1—C6	1.408 (2)	C11—H11A	0.9800
C2—C3	1.386 (3)	C11—H11B	0.9800
C2—H2A	0.9500	C11—H11C	0.9800
C3—C4	1.381 (3)		
C9—S1—C10	101.07 (10)	O1—C7—H7A	109.5
C9—S2—C11	104.77 (10)	O1—C7—H7B	109.5
C1—O1—C7	118.23 (16)	H7A—C7—H7B	109.5
C8—N1—N2	119.76 (16)	O1—C7—H7C	109.5
C8—N1—H1N	117.2 (19)	H7A—C7—H7C	109.5
N2—N1—H1N	122.7 (19)	H7B—C7—H7C	109.5
C9—N2—N1	115.35 (16)	O2—C8—N1	122.69 (16)
O1—C1—C2	122.80 (17)	O2—C8—C6	120.62 (16)
O1—C1—C6	117.25 (16)	N1—C8—C6	116.69 (15)
C2—C1—C6	119.95 (18)	N2—C9—S1	119.27 (15)
C3—C2—C1	120.40 (18)	N2—C9—S2	123.33 (14)
C3—C2—H2A	119.8	S1—C9—S2	117.39 (11)
C1—C2—H2A	119.8	S1—C10—H10A	109.5
C4—C3—C2	120.53 (18)	S1—C10—H10B	109.5
C4—C3—H3A	119.7	H10A—C10—H10B	109.5
C2—C3—H3A	119.7	S1—C10—H10C	109.5
C3—C4—C5	118.7 (2)	H10A—C10—H10C	109.5
C3—C4—H4A	120.7	H10B—C10—H10C	109.5
C5—C4—H4A	120.7	S2—C11—H11A	109.5
C4—C5—C6	122.66 (19)	S2—C11—H11B	109.5
C4—C5—H5A	118.7	H11A—C11—H11B	109.5

C6—C5—H5A	118.7	S2—C11—H11C	109.5
C5—C6—C1	117.76 (16)	H11A—C11—H11C	109.5
C5—C6—C8	115.35 (16)	H11B—C11—H11C	109.5
C1—C6—C8	126.88 (16)		
C8—N1—N2—C9	170.57 (17)	C2—C1—C6—C8	178.17 (18)
C7—O1—C1—C2	−5.0 (3)	N2—N1—C8—O2	−4.3 (3)
C7—O1—C1—C6	174.99 (17)	N2—N1—C8—C6	176.21 (15)
O1—C1—C2—C3	179.51 (18)	C5—C6—C8—O2	−1.7 (3)
C6—C1—C2—C3	−0.5 (3)	C1—C6—C8—O2	179.63 (19)
C1—C2—C3—C4	1.0 (3)	C5—C6—C8—N1	177.76 (17)
C2—C3—C4—C5	−0.4 (3)	C1—C6—C8—N1	−0.9 (3)
C3—C4—C5—C6	−0.6 (3)	N1—N2—C9—S1	176.15 (13)
C4—C5—C6—C1	1.0 (3)	N1—N2—C9—S2	−4.5 (3)
C4—C5—C6—C8	−177.78 (18)	C10—S1—C9—N2	−1.1 (2)
O1—C1—C6—C5	179.54 (16)	C10—S1—C9—S2	179.49 (14)
C2—C1—C6—C5	−0.5 (3)	C11—S2—C9—N2	173.48 (18)
O1—C1—C6—C8	−1.8 (3)	C11—S2—C9—S1	−7.15 (15)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1	0.78 (3)	1.97 (3)	2.627 (2)	141 (2)
C10—H10*A*···O2^{i}	0.98	2.37	3.326 (3)	166
C11—H11*A*···O2^{ii}	0.98	2.61	3.341 (3)	131

Symmetry codes: (i) −*x*+1/2, *y*−1/2, −*z*+1/2; (ii) *x*+1, *y*, *z*.