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Benzyl *N*′-(2-methoxybenzoyl)hydrazinecarbodithioate

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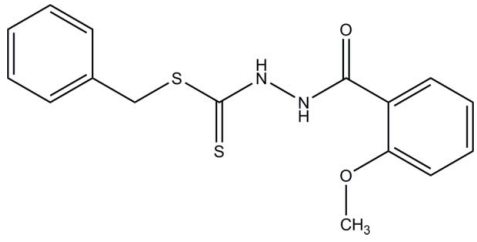
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.004 Å; R factor = 0.083; wR factor = 0.273; data-to-parameter ratio = 27.3.

The title dithio ester, $C_{16}H_{16}N_2O_2S_2$, was synthesized by the reaction of potassium *N*′-(2-methoxybenzoyl)hydrazinecarbodithioate and benzyl chloride in chloroform. The dihedral angle between the 2-methoxyphenyl ring and the benzyl ring is 85.06 (2) Å. In the crystal structure, intra- and intermolecular hydrogen bonding stabilizes the molecule and the crystal packing.

Related literature

For related literature, see: Trarafder *et al.* (2001); Bhardawaj *et al.* (1987); Singh & Gupta (2002); Wu *et al.* (2000); Singh *et al.* (2007).



Experimental

Crystal data

$C_{16}H_{16}N_2O_2S_2$
M_r = 332.43
Triclinic, $P\overline{1}$
a = 7.493 (2) Å
b = 10.230 (3) Å
c = 11.212 (4) Å
α = 74.56 (3)°
β = 81.49 (3)°
γ = 77.61 (2)°
V = 805.3 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.34 mm^{-1}
T = 295 (2) K
0.55 × 0.37 × 0.21 mm

Data collection

Oxford Diffraction Gemini diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
T_{min} = 0.332, T_{max} = 1.000 (expected range = 0.309–0.931)
23923 measured reflections
5465 independent reflections
2864 reflections with $I > 2\sigma(I)$
R_{int} = 0.070

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.083
$wR(F^2)$ = 0.273
S = 1.07
5465 reflections
200 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.83 e Å^{-3}
$\Delta\rho_{min}$ = −0.57 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1D···O1	0.86	1.88	2.574 (3)	136
N2—H2A···O2^{i}	0.86	1.94	2.786 (3)	167

Symmetry code: (i) $-x, -y, -z+2$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2591).

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supplementary materials

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Benzyl *N*'-(2-methoxybenzoyl)hydrazinecarbodithioate

N. K. Singh, M. Singh and R. J. Butcher

Comment

Dithioligands are very promising compounds from the view point of coordination chemistry because of their ability towards complexation and involvement in a wide range of biological (Trarafder *et al.*, 2001, Bhardawaj & Musker, 1987) and non-biological processes (Singh & Gupta, 2002). As not much data is available on the synthesis and structural characterization of *N*'-acylhydrazine carbodithio acid esters, the syntheses and elucidation of crystal structure of compound (I) has been undertaken. The molecular structure of (I) together with the atom labeling scheme, is shown in Fig 1. In the title compound, the *o*-methoxyphenyl ring unit and benzyl ring are in two different planes. The dihedral angle between *o*-methoxyphenyl ring and benzyl ring is 85.06 (2) Å. Hydrazinic atoms H1D and H2A are *trans* to each other, as are the C(9)—S(1) and C(8)—O(2) groups [torsional angles, N2—N1—C8—C7 and C10—S2—C9-(N2) = −173.3 (2)° and 170.75 (19)°, respectively]. The C—S and C=S bonds present in the molecule are 1.656 Å and 1.740 Å (3) which agree well with equivalent bonds, being intermediate between 1.82 Å for a C—S single bond and 1.56 Å for a C=S double bond (Wu *et al.*, 2000). The C—N bond distance is 1.375 (2) Å, which is also intermediate between C—N (1.450 Å) and C=N (1.250 Å). The intermediate bond distances in compound (I) illustrate the extensive electron delocalization which provides stability to the molecule. The three dimensional structure of (I) demonstrates that atoms O, N and S are available as donor sites for coordination to metals either as a tridentate neutral or mononegative ligand. The H3A hydrogen of two different *o*-methoxyphenyl rings form weak Van der Waals interaction with each other (H3A···H3A = 2.398 Å).

Experimental

The potassium[*N*'-(2-methoxy-benzoyl)-hydrazinecarbodithioate] was synthesized according to earlier reported literature method (Singh *et al.*, 2007). Compound (I) was synthesized by the reaction of benzyl chloride (1.7 ml, 14.26 mmol) suspension of to a freshly prepared potassium[*N*'-(2-methoxy-benzoyl)-hydrazinecarbodithioate] (4 g, 14.26 mmol) in choloroform (15 ml) and stirring the reaction mixture continuously for 2 h at room temperature. The resulting solution was filtered and kept in a freezer for crystallization. White plate-shaped single crystals of (I) (m.p. 453 K) suitable for X-ray analysis were obtained by slow evaporation of a chloroform solution over a period of 1 d. (yield 2.08 g, 52%). Analysis found (%) for $C_{16}H_{16}N_2O_2S_2$ (332.43): C, 57.83; H, 4.90; N, 8.39; S, 19.30. Calculated (%): C, 57.81; H, 4.85; N, 8.43; S, 19.29.

Refinement

All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry with C—H distances of 0.96Å and U_{iso} (H) = 1.5 U_{eq} (C), but each group was allowed to rotate freely about its C—C bond. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with an N—H distance of 0.86 Å and C—H distances in the range of 0.93–0.97 Å and U_{iso}(H) = 1.2 U_{eq} (C, N).

Figures

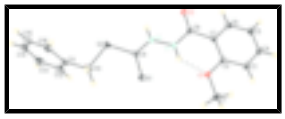

Fig. 1. The molecular structure of (I), showing the atom numbering scheme with displacement ellipsoid drawn at the 20% probability level. The dashed line indicates intramolecular hydrogen bonding NH···O.

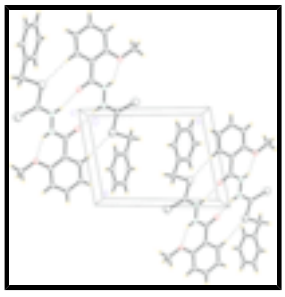

Fig. 2. The crystal packing of (I), showing hydrogen bonding interactions by dashed lines.

Benzyl *N*'-(2-methoxybenzoyl)hydrazinecarbodithioate

Crystal data

$C_{16}H_{16}N_2O_2S_2$	F_{000} = 348
M_r = 332.43	D_x = 1.371 Mg m^{-3}
Triclinic, $P\overline{1}$	Melting point: 453 K
a = 7.493 (2) Å	Mo $K\alpha$ radiation λ = 0.71073 Å
b = 10.230 (3) Å	Cell parameters from 8677 reflections
c = 11.212 (4) Å	θ = 4.7–32.4º
α = 74.56 (3)º	μ = 0.34 mm^{-1}
β = 81.49 (3)º	T = 295 (2) K
γ = 77.61 (2)º	Irregular chunk, pale yellow
V = 805.3 (4) Å^3	0.55 × 0.37 × 0.21 mm
Z = 2	

Data collection

Oxford Diffraction Gemini diffractometer	R_{int} = 0.070
Radiation source: fine-focus sealed tube	θ_{max} = 32.6º
Monochromator: graphite	θ_{min} = 4.8º
T = 295(2) K	h = −11→11
phi and ω scans	k = −15→15
Absorption correction: multi-scan (Crysalis RED; Oxford Diffraction, 2007)	l = −16→16
T_{min} = 0.332, T_{max} = 1.000	2 standard reflections
23923 measured reflections	every 50 reflections
5465 independent reflections	intensity decay: <2%
2864 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.083$

$wR(F^2) = 0.273$

$S = 1.07$

5465 reflections

200 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1384P)^2 + 0.286P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.83$ e Å^{-3}

$\Delta\rho_{min} = -0.57$ e Å^{-3}

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}
S1	−0.09425 (9)	0.45170 (6)	0.72229 (6)	0.06447 (19)
S2	0.23392 (9)	0.22193 (7)	0.71650 (6)	0.0718 (2)
O1	−0.5450 (2)	0.39719 (18)	0.90884 (18)	0.0693 (5)
O2	−0.2038 (2)	0.03963 (18)	1.06503 (17)	0.0718 (5)
N1	−0.2336 (2)	0.2310 (2)	0.91251 (19)	0.0581 (5)
H1D	−0.3015	0.3076	0.8796	0.070*
N2	−0.0554 (2)	0.19913 (19)	0.86344 (18)	0.0556 (5)
H2A	0.0097	0.1193	0.8911	0.067*
C1	−0.6582 (4)	0.5247 (3)	0.8573 (3)	0.0772 (8)
H1A	−0.5846	0.5834	0.7986	0.116*
H1B	−0.7151	0.5688	0.9225	0.116*
H1C	−0.7513	0.5078	0.8158	0.116*
C2	−0.6188 (3)	0.3006 (2)	0.9996 (2)	0.0545 (5)
C3	−0.8027 (3)	0.3183 (3)	1.0435 (3)	0.0688 (7)
H3A	−0.8816	0.3992	1.0103	0.083*
C4	−0.8691 (4)	0.2182 (3)	1.1348 (3)	0.0752 (8)
H4A	−0.9929	0.2322	1.1635	0.090*
C5	−0.7563 (4)	0.0969 (3)	1.1854 (3)	0.0718 (8)
H5A	−0.8031	0.0292	1.2477	0.086*
C6	−0.5734 (3)	0.0775 (3)	1.1422 (2)	0.0627 (6)
H6A	−0.4965	−0.0045	1.1753	0.075*

C7	−0.5017 (3)	0.1778 (2)	1.0502 (2)	0.0480 (5)
C8	−0.3025 (3)	0.1435 (2)	1.0113 (2)	0.0493 (5)
C9	0.0156 (3)	0.2919 (2)	0.77336 (19)	0.0490 (5)
C10	0.2901 (4)	0.3524 (3)	0.5800 (2)	0.0709 (7)
H10A	0.1953	0.3775	0.5235	0.085*
H10B	0.3039	0.4345	0.6029	0.085*
C11	0.4685 (3)	0.2867 (3)	0.5222 (2)	0.0592 (6)
C12	0.4727 (5)	0.2113 (3)	0.4372 (3)	0.0822 (9)
H12A	0.3641	0.2046	0.4103	0.099*
C13	0.6400 (7)	0.1448 (4)	0.3915 (3)	0.1008 (12)
H13A	0.6442	0.0917	0.3352	0.121*
C14	0.7985 (5)	0.1580 (4)	0.4300 (3)	0.1010 (13)
H14A	0.9110	0.1138	0.3995	0.121*
C15	0.7933 (5)	0.2343 (5)	0.5116 (4)	0.1004 (12)
H15A	0.9018	0.2432	0.5370	0.120*
C16	0.6313 (4)	0.2976 (4)	0.5564 (3)	0.0786 (8)
H16A	0.6298	0.3505	0.6124	0.094*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0643 (3)	0.0451 (3)	0.0641 (4)	−0.0005 (3)	−0.0045 (3)	0.0123 (3)
S2	0.0597 (3)	0.0582 (3)	0.0619 (4)	0.0051 (3)	0.0137 (3)	0.0232 (3)
O1	0.0521 (8)	0.0509 (9)	0.0782 (11)	0.0065 (7)	−0.0011 (8)	0.0145 (8)
O2	0.0511 (8)	0.0573 (9)	0.0712 (11)	0.0083 (7)	0.0069 (8)	0.0244 (8)
N1	0.0426 (9)	0.0505 (10)	0.0587 (11)	0.0034 (7)	0.0018 (8)	0.0118 (8)
N2	0.0448 (9)	0.0464 (9)	0.0555 (10)	0.0008 (7)	0.0041 (8)	0.0096 (8)
C1	0.0713 (15)	0.0486 (13)	0.0913 (19)	0.0108 (11)	−0.0183 (14)	0.0063 (12)
C2	0.0480 (10)	0.0509 (11)	0.0552 (12)	0.0041 (9)	−0.0058 (9)	−0.0068 (9)
C3	0.0462 (11)	0.0684 (15)	0.0762 (16)	0.0077 (11)	−0.0014 (11)	−0.0077 (13)
C4	0.0481 (12)	0.0830 (18)	0.0763 (17)	−0.0001 (12)	0.0091 (12)	−0.0061 (14)
C5	0.0541 (12)	0.0755 (16)	0.0683 (16)	−0.0107 (12)	0.0121 (11)	0.0016 (13)
C6	0.0549 (12)	0.0566 (13)	0.0601 (14)	−0.0041 (10)	0.0017 (10)	0.0050 (10)
C7	0.0426 (9)	0.0457 (10)	0.0469 (10)	0.0000 (8)	−0.0032 (8)	−0.0034 (8)
C8	0.0420 (9)	0.0445 (10)	0.0486 (11)	−0.0009 (8)	0.0008 (8)	0.0021 (8)
C9	0.0505 (10)	0.0459 (10)	0.0404 (10)	−0.0027 (8)	−0.0067 (8)	0.0035 (8)
C10	0.0742 (15)	0.0591 (14)	0.0562 (14)	−0.0076 (12)	0.0083 (12)	0.0141 (11)
C11	0.0666 (13)	0.0557 (12)	0.0432 (11)	−0.0200 (10)	0.0063 (10)	0.0092 (9)
C12	0.104 (2)	0.0827 (19)	0.0594 (16)	−0.0291 (17)	−0.0100 (15)	−0.0062 (14)
C13	0.146 (3)	0.077 (2)	0.0666 (18)	−0.009 (2)	0.012 (2)	−0.0177 (16)
C14	0.088 (2)	0.101 (3)	0.075 (2)	0.0041 (19)	0.0265 (17)	0.0102 (18)
C15	0.0666 (17)	0.122 (3)	0.097 (3)	−0.0169 (19)	0.0049 (17)	−0.006 (2)
C16	0.0774 (17)	0.0896 (19)	0.0693 (17)	−0.0286 (15)	0.0037 (14)	−0.0154 (15)

Geometric parameters (Å, °)

S1—C9	1.656 (2)	C5—C6	1.375 (4)
S2—C9	1.740 (2)	C5—H5A	0.9300
S2—C10	1.807 (3)	C6—C7	1.383 (3)

O1—C2	1.361 (3)	C6—H6A	0.9300
O1—C1	1.422 (3)	C7—C8	1.485 (3)
O2—C8	1.222 (3)	C10—C11	1.500 (4)
N1—C8	1.340 (3)	C10—H10A	0.9700
N1—N2	1.372 (3)	C10—H10B	0.9700
N1—H1D	0.8600	C11—C16	1.367 (4)
N2—C9	1.323 (3)	C11—C12	1.370 (4)
N2—H2A	0.8600	C12—C13	1.388 (5)
C1—H1A	0.9600	C12—H12A	0.9300
C1—H1B	0.9600	C13—C14	1.367 (6)
C1—H1C	0.9600	C13—H13A	0.9300
C2—C3	1.383 (3)	C14—C15	1.343 (6)
C2—C7	1.401 (3)	C14—H14A	0.9300
C3—C4	1.361 (4)	C15—C16	1.342 (5)
C3—H3A	0.9300	C15—H15A	0.9300
C4—C5	1.376 (4)	C16—H16A	0.9300
C4—H4A	0.9300		
C9—S2—C10	104.13 (12)	C2—C7—C8	125.06 (19)
C2—O1—C1	119.7 (2)	O2—C8—N1	120.48 (19)
C8—N1—N2	120.43 (17)	O2—C8—C7	122.33 (19)
C8—N1—H1D	119.8	N1—C8—C7	117.18 (17)
N2—N1—H1D	119.8	N2—C9—S1	123.36 (17)
C9—N2—N1	119.61 (17)	N2—C9—S2	110.94 (15)
C9—N2—H2A	120.2	S1—C9—S2	125.69 (13)
N1—N2—H2A	120.2	C11—C10—S2	104.53 (17)
O1—C1—H1A	109.5	C11—C10—H10A	111.0
O1—C1—H1B	109.5	S2—C10—H10A	110.9
H1A—C1—H1B	109.5	C11—C10—H10B	110.9
O1—C1—H1C	109.5	S2—C10—H10B	110.7
H1A—C1—H1C	109.5	H10A—C10—H10B	108.8
H1B—C1—H1C	109.5	C16—C11—C12	118.4 (3)
O1—C2—C3	123.0 (2)	C16—C11—C10	120.3 (3)
O1—C2—C7	117.93 (19)	C12—C11—C10	121.3 (3)
C3—C2—C7	119.0 (2)	C11—C12—C13	119.6 (3)
C4—C3—C2	120.6 (2)	C11—C12—H12A	120.2
C4—C3—H3A	119.7	C13—C12—H12A	120.2
C2—C3—H3A	119.7	C14—C13—C12	119.4 (4)
C3—C4—C5	121.2 (2)	C14—C13—H13A	120.3
C3—C4—H4A	119.4	C12—C13—H13A	120.3
C5—C4—H4A	119.4	C15—C14—C13	120.5 (3)
C6—C5—C4	118.8 (3)	C15—C14—H14A	119.7
C6—C5—H5A	120.6	C13—C14—H14A	119.7
C4—C5—H5A	120.6	C16—C15—C14	119.9 (4)
C5—C6—C7	121.2 (2)	C16—C15—H15A	120.0
C5—C6—H6A	119.4	C14—C15—H15A	120.0
C7—C6—H6A	119.4	C15—C16—C11	122.0 (3)
C6—C7—C2	119.1 (2)	C15—C16—H16A	119.0
C6—C7—C8	115.81 (19)	C11—C16—H16A	119.0

C8—N1—N2—C9	−173.7 (2)	C6—C7—C8—N1	172.1 (2)
C1—O1—C2—C3	1.6 (4)	C2—C7—C8—N1	−6.6 (4)
C1—O1—C2—C7	−178.4 (3)	N1—N2—C9—S1	4.9 (3)
O1—C2—C3—C4	−179.8 (3)	N1—N2—C9—S2	−174.10 (18)
C7—C2—C3—C4	0.2 (4)	C10—S2—C9—N2	170.75 (19)
C2—C3—C4—C5	−0.4 (5)	C10—S2—C9—S1	−8.2 (2)
C3—C4—C5—C6	0.0 (5)	C9—S2—C10—C11	−173.74 (19)
C4—C5—C6—C7	0.5 (5)	S2—C10—C11—C16	−89.0 (3)
C5—C6—C7—C2	−0.7 (4)	S2—C10—C11—C12	89.1 (3)
C5—C6—C7—C8	−179.6 (3)	C16—C11—C12—C13	2.1 (4)
O1—C2—C7—C6	−179.6 (2)	C10—C11—C12—C13	−176.0 (3)
C3—C2—C7—C6	0.3 (4)	C11—C12—C13—C14	−1.4 (5)
O1—C2—C7—C8	−0.9 (4)	C12—C13—C14—C15	0.1 (5)
C3—C2—C7—C8	179.1 (2)	C13—C14—C15—C16	0.4 (6)
N2—N1—C8—O2	5.8 (4)	C14—C15—C16—C11	0.4 (6)
N2—N1—C8—C7	−173.3 (2)	C12—C11—C16—C15	−1.6 (5)
C6—C7—C8—O2	−7.0 (4)	C10—C11—C16—C15	176.5 (3)
C2—C7—C8—O2	174.2 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1D···O1	0.86	1.88	2.574 (3)	136
N2—H2A···O2^{i}	0.86	1.94	2.786 (3)	167

Symmetry codes: (i) −*x*, −*y*, −*z*+2.

Fig. 1

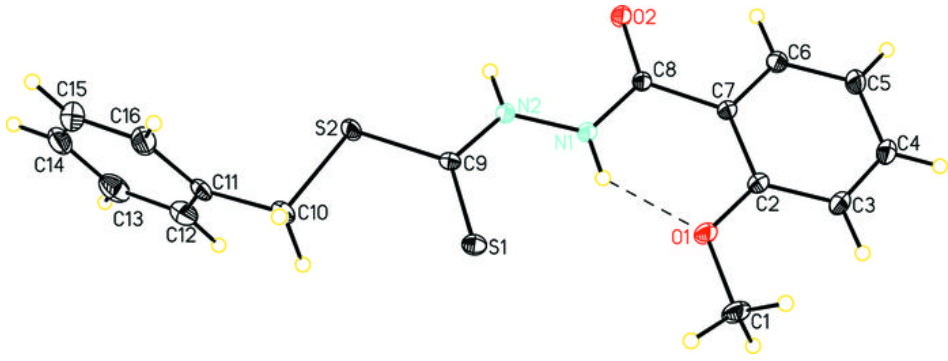
O2
C6
C8
C7
C5
C15
C16
N2
S2
N1
C4
C14
C9
C11
C2
C3
C13
C10
C12
O1
S1
C1

Fig. 2