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rac-1-(5-Bromo-2-hydroxyphenyl)-1-oxopropan-2-yl morpholine-4-carbodithioate

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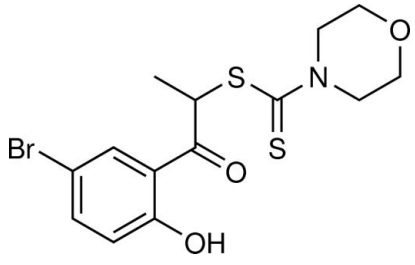
Key indicators: single-crystal X-ray study; T = 153 K; mean σ(C–C) = 0.004 Å; R factor = 0.045; wR factor = 0.102; data-to-parameter ratio = 21.8.

In the racemic title compound, $C_{14}H_{16}BrNO_3S_2$, synthesized from the corresponding ω-bromopropiophenone, the dihedral angle between the plane of the phenol group and that of the planar section [maximum deviation = 0.040 (2) Å] of the morpholine-4-carbodithiolate moiety is 76.36 (10)°. A strong intramolecular phenol O—H···O hydrogen bond if present in the molecule. In the crystal, only weak C—H···S and C—H···O interactions are found.

Related literature

For the synthesis and applications of dithiocarbamates, see: Buu-Hoi & Lavit (1955); WHO (1998). For applications of 1,3-dithiolium salts, see: Narita & Pittman (1976); Birsa & Asaftei (2008). For the structure of a related morpholine-4-carbodithioate, see: Bahrin *et al.* (2012).



Experimental

Crystal data

$C_{14}H_{16}BrNO_3S_2$
M_r = 390.31
Monoclinic, $P2_1/c$
a = 11.182 (2) Å
b = 19.660 (4) Å
c = 7.4593 (15) Å
β = 105.44 (3)°
V = 1580.6 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.87 mm^{-1}
T = 153 K
0.54 × 0.48 × 0.30 mm

Data collection

Stoe IPDS 2T area-detector diffractometer
Absorption correction: for a sphere [modification of the interpolation procedure of Dwiggins (1975)]
T_{min} = 0.114, T_{max} = 0.140
17019 measured reflections
4246 independent reflections
3807 reflections with $I > 2\sigma(I)$
R_{int} = 0.072

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.102
S = 1.16
4246 reflections
195 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.71 e Å^{-3}
$\Delta\rho_{min}$ = −0.78 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2	0.76 (4)	1.86 (4)	2.558 (3)	151 (5)
C4—H4···S2^{i}	0.95	2.79	3.712 (3)	164
C3—H3···O3^{ii}	0.95	2.51	3.443 (4)	168
C12—H12B···O1^{iii}	0.99	2.46	3.454 (4)	178

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

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2265).

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S1. Comment

Dithiocarbamates have important uses as chemical precursors, effluent additives, agricultural pesticides, and in experimental and clinical medicine (WHO, 1998). In particular, phenacyldithiocarbamates are important precursors of 1,3-dithiolium salts (Birsa & Asaftei, 2008), which in turn are well known precursors of tetrathiafulvalenes (Narita & Pittman, 1976). The racemic title compound $C_{14}H_{16}BrNO_3S_2$ has been synthesized by the reaction of 2-bromo-1-(5-bromo-2-hydroxyphenyl)-propan-1-one (Buu-Hoi & Lavit, 1955) with a salt of morpholine-4-carbodithioate. In this compound (Fig. 1), the dihedral angle between the phenolic ring system and the plane defined by atoms S1,S2,C9,C10,C13 of the morpholine-4-carbodithiolate moiety is 76.36 (10)°. The maximum deviation from the least-squares plane to this fragment is 0.040 (2) Å (C9). A strong intramolecular hydrogen bond between the phenolic O1—H group and a carbonyl O-atom acceptor atom of the side chain (O2) is present (Table 1). In the crystal there is a weak intermolecular C4—H···S2^{i} association [3.712 (3)Å] and weak C3—H···O3^{ii} and C12—H···O1^{iii} hydrogen bonds [3.443 (4) and 3.454(4 Å, respectively] (for symmetry codes, see Table 1).

S2. Experimental

To a solution of 0.924 g (3 mmol) 2-bromo-1-(5-bromo-2-hydroxyphenyl)-propan-1-one (Buu-Hoi & Lavit, 1955) in 10 ml of acetone was added a solution of 0.75 g (3 mmol) morpholinium morpholine-4-carbodithioate in 10 ml acetone-water (1:1). The reaction mixture was heated at reflux for 10 min, cooled to room temperature and then poured into water. The precipitate was filtered, washed with water and dried (m.p. 412–413 K). IR (ATR): ν_{max} 2852, 1643, 1466, 1424, 1258, 1228, 1111, 999, 624, 543 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d6): δ = 1.57 (d, 3H, CH3), 3.74 (m, 4H, 2CH2-O), 4.09 (m, 4H, 2CH2-N), 5.75 (q, 1H, CH), 6.88 (d, 3 J=8.0 Hz, 1H), 7.53 (dd, 3 J=8.0 Hz, 4 J=1.1 Hz, 1H), 8.04 (d, 4 J=1.1 Hz, 1H), 11.04 (s, 1H, OH). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d6): δ = 17.2 (*q*), 51.2 (*d*), 52.3 (*t*), 66.7 (*t*), 111.3 (*s*), 119.8 (*d*), 121.1 (*s*), 133.0 (*d*), 133.3 (*d*), 162.4 (*s*), 194.4 (*s*), 203.5 (*s*).

S3. Refinement

The C-bound H-atoms were included at calculated positions and treated using a riding model, with aromatic C—H = 0.95 Å, methylene C—H = 0.99 Å and methine C—H = 1.00 Å and U_{iso}(H) = 1.2U_{eq}(C), or with methyl C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C). The phenolic H-atom (H1) was free refined.

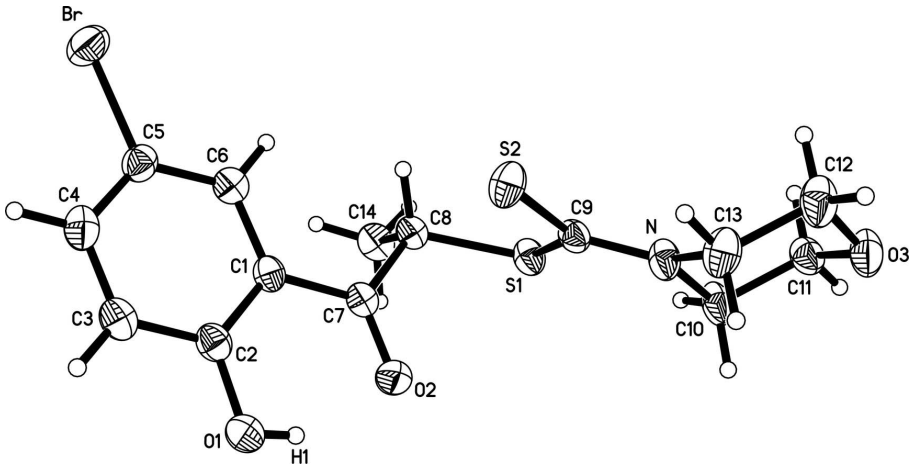

Figure 1

Molecular conformation and atom numbering scheme for the title compound, with thermal ellipsoids drawn at the 50% probability level.

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Crystal data

$C_{14}H_{16}BrNO_3S_2$
$M_r = 390.31$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 11.182$ (2) Å
$b = 19.660$ (4) Å
$c = 7.4593$ (15) Å
$\beta = 105.44$ (3)°
$V = 1580.6$ (5) Å^3
$Z = 4$
$F(000) = 792$
$D_x = 1.640$ Mg m^{-3}
Melting point = 412–413 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 26120 reflections
$\theta = 2.2$–29.7°
$\mu = 2.87$ mm^{-1}
$T = 153$ K
Prism, colourless
0.54 × 0.48 × 0.30 mm

Data collection

Stoe IPDS 2T area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 6.67 pixels mm^{-1}
rotation method scans
Absorption correction: for a sphere [modification of the interpolation procedure of Dwiggins (1975)]
$T_{min} = 0.114$, $T_{max} = 0.140$
17019 measured reflections
4246 independent reflections
3807 reflections with $I > 2\sigma(I)$
$R_{int} = 0.072$
$\theta_{max} = 29.2°$, $\theta_{min} = 2.8°$
$h = -15\rightarrow13$
$k = -25\rightarrow26$
$l = -10\rightarrow10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.102$
$S = 1.16$
4246 reflections
195 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2 + 1.2363P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -0.78$ e Å^{-3}

Special details

Experimental. Absorption correction: interpolation using International Tables Vol C, Table 6.3.3.3 for values of muR in the range 0-2.5, and International Tables Vol. II, Table 5.3.6 B for μR in the range 2.6-10.0. The interpolation procedure (Dwiggins, 1975) was used with some modification.

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 $F^2 > \sigma(F^2)$ 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}
N	0.7046 (2)	0.59260 (10)	−0.3669 (3)	0.0291 (4)
Br	0.94733 (3)	0.200387 (14)	0.15953 (5)	0.04007 (10)
S1	0.82823 (6)	0.55807 (3)	−0.03082 (8)	0.02727 (13)
S2	0.72078 (6)	0.45824 (3)	−0.33614 (9)	0.03161 (15)
O1	0.50712 (18)	0.37914 (11)	0.1313 (3)	0.0344 (4)
H1	0.525 (4)	0.416 (2)	0.120 (6)	0.059 (13)*
O2	0.63809 (17)	0.48119 (9)	0.0864 (3)	0.0316 (4)
O3	0.6883 (2)	0.70107 (9)	−0.6200 (3)	0.0378 (5)
C1	0.7188 (2)	0.36994 (12)	0.1107 (3)	0.0243 (4)
C2	0.6083 (2)	0.34177 (13)	0.1327 (3)	0.0269 (5)
C3	0.5990 (3)	0.27144 (14)	0.1556 (4)	0.0320 (5)
H3	0.5233	0.2522	0.1665	0.038*
C4	0.6994 (3)	0.23020 (13)	0.1624 (4)	0.0320 (5)
H4	0.6934	0.1826	0.1794	0.038*
C5	0.8095 (2)	0.25820 (12)	0.1445 (3)	0.0281 (5)
C6	0.8199 (2)	0.32679 (13)	0.1174 (3)	0.0269 (5)
H6	0.8955	0.3450	0.1031	0.032*
C7	0.7261 (2)	0.44422 (12)	0.0859 (3)	0.0246 (4)
C8	0.8494 (2)	0.47533 (12)	0.0777 (3)	0.0255 (4)
H8	0.8923	0.4444	0.0084	0.031*
C9	0.7432 (2)	0.53841 (11)	−0.2621 (3)	0.0238 (4)
C10	0.7202 (3)	0.66338 (12)	−0.3028 (4)	0.0359 (6)
H10A	0.7798	0.6655	−0.1782	0.043*
H10B	0.6397	0.6816	−0.2927	0.043*
C11	0.7672 (3)	0.70563 (12)	−0.4379 (4)	0.0311 (5)
H11A	0.7733	0.7537	−0.3972	0.037*
H11B	0.8513	0.6900	−0.4379	0.037*
C12	0.6805 (3)	0.63236 (14)	−0.6823 (4)	0.0393 (7)
H12A	0.7643	0.6159	−0.6817	0.047*

H12B	0.6274	0.6299	−0.8116	0.047*
C13	0.6270 (3)	0.58721 (13)	−0.5588 (4)	0.0353 (6)
H13A	0.5411	0.6015	−0.5652	0.042*
H13B	0.6249	0.5394	−0.6016	0.042*
C14	0.9305 (3)	0.48568 (15)	0.2771 (4)	0.0332 (5)
H14A	0.8848	0.5126	0.3476	0.050*
H14B	1.0067	0.5097	0.2740	0.050*
H14C	0.9517	0.4413	0.3372	0.050*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N	0.0470 (13)	0.0183 (9)	0.0238 (9)	−0.0032 (8)	0.0125 (9)	−0.0015 (7)
Br	0.03949 (16)	0.03294 (15)	0.04765 (17)	0.00946 (11)	0.01139 (12)	0.00128 (11)
S1	0.0348 (3)	0.0231 (3)	0.0248 (3)	−0.0061 (2)	0.0095 (2)	−0.0022 (2)
S2	0.0381 (3)	0.0189 (2)	0.0340 (3)	−0.0042 (2)	0.0029 (3)	−0.0027 (2)
O1	0.0267 (9)	0.0330 (10)	0.0462 (11)	−0.0017 (7)	0.0143 (8)	0.0047 (8)
O2	0.0280 (9)	0.0295 (9)	0.0393 (10)	0.0013 (7)	0.0127 (8)	0.0029 (7)
O3	0.0579 (13)	0.0268 (9)	0.0293 (9)	0.0021 (8)	0.0125 (9)	0.0056 (7)
C1	0.0268 (11)	0.0257 (10)	0.0202 (9)	−0.0017 (8)	0.0058 (8)	0.0018 (8)
C2	0.0256 (11)	0.0304 (11)	0.0241 (10)	−0.0029 (9)	0.0056 (9)	0.0017 (9)
C3	0.0311 (12)	0.0326 (12)	0.0329 (12)	−0.0058 (10)	0.0096 (10)	0.0015 (10)
C4	0.0391 (14)	0.0263 (11)	0.0300 (12)	−0.0037 (10)	0.0080 (11)	0.0019 (9)
C5	0.0326 (12)	0.0269 (11)	0.0242 (11)	0.0037 (9)	0.0063 (9)	0.0013 (9)
C6	0.0257 (11)	0.0294 (11)	0.0245 (10)	−0.0014 (9)	0.0049 (9)	−0.0002 (9)
C7	0.0247 (11)	0.0260 (10)	0.0232 (10)	−0.0024 (8)	0.0067 (8)	0.0014 (8)
C8	0.0254 (11)	0.0263 (10)	0.0256 (10)	−0.0020 (9)	0.0082 (9)	0.0013 (8)
C9	0.0271 (11)	0.0206 (9)	0.0263 (10)	−0.0040 (8)	0.0117 (9)	−0.0005 (8)
C10	0.0671 (19)	0.0182 (10)	0.0289 (12)	−0.0029 (11)	0.0240 (13)	0.0000 (9)
C11	0.0418 (14)	0.0247 (11)	0.0306 (12)	−0.0031 (10)	0.0161 (11)	−0.0006 (9)
C12	0.062 (2)	0.0291 (12)	0.0234 (11)	0.0014 (12)	0.0061 (12)	−0.0007 (9)
C13	0.0399 (14)	0.0272 (12)	0.0335 (13)	−0.0032 (10)	0.0006 (11)	0.0011 (10)
C14	0.0287 (12)	0.0398 (14)	0.0292 (11)	−0.0039 (10)	0.0044 (10)	0.0007 (10)

Geometric parameters (Å, º)

N—C9	1.324 (3)	C4—H4	0.9500
N—C10	1.467 (3)	C5—C6	1.373 (3)
N—C13	1.467 (3)	C6—H6	0.9500
Br—C5	1.894 (3)	C7—C8	1.524 (3)
S1—C9	1.776 (2)	C8—C14	1.536 (3)
S1—C8	1.804 (2)	C8—H8	1.0000
S2—C9	1.667 (2)	C10—C11	1.504 (3)
O1—C2	1.346 (3)	C10—H10A	0.9900
O1—H1	0.77 (4)	C10—H10B	0.9900
O2—C7	1.224 (3)	C11—H11A	0.9900
O3—C11	1.412 (3)	C11—H11B	0.9900
O3—C12	1.424 (3)	C12—C13	1.512 (4)

C1—C6	1.403 (3)	C12—H12A	0.9900
C1—C2	1.404 (3)	C12—H12B	0.9900
C1—C7	1.477 (3)	C13—H13A	0.9900
C2—C3	1.400 (4)	C13—H13B	0.9900
C3—C4	1.375 (4)	C14—H14A	0.9800
C3—H3	0.9500	C14—H14B	0.9800
C4—C5	1.387 (4)	C14—H14C	0.9800

C9—N—C10	125.4 (2)	N—C9—S2	124.63 (19)
C9—N—C13	122.2 (2)	N—C9—S1	113.86 (17)
C10—N—C13	112.0 (2)	S2—C9—S1	121.47 (14)
C9—S1—C8	102.22 (11)	N—C10—C11	109.7 (2)
C2—O1—H1	106 (3)	N—C10—H10A	109.7
C11—O3—C12	110.0 (2)	C11—C10—H10A	109.7
C6—C1—C2	118.9 (2)	N—C10—H10B	109.7
C6—C1—C7	122.1 (2)	C11—C10—H10B	109.7
C2—C1—C7	118.9 (2)	H10A—C10—H10B	108.2
O1—C2—C3	116.8 (2)	O3—C11—C10	111.7 (2)
O1—C2—C1	123.2 (2)	O3—C11—H11A	109.3
C3—C2—C1	120.0 (2)	C10—C11—H11A	109.3
C4—C3—C2	120.0 (2)	O3—C11—H11B	109.3
C4—C3—H3	120.0	C10—C11—H11B	109.3
C2—C3—H3	120.0	H11A—C11—H11B	107.9
C3—C4—C5	120.0 (2)	O3—C12—C13	111.0 (2)
C3—C4—H4	120.0	O3—C12—H12A	109.4
C5—C4—H4	120.0	C13—C12—H12A	109.4
C6—C5—C4	121.1 (2)	O3—C12—H12B	109.4
C6—C5—Br	119.9 (2)	C13—C12—H12B	109.4
C4—C5—Br	119.03 (19)	H12A—C12—H12B	108.0
C5—C6—C1	120.0 (2)	N—C13—C12	109.0 (2)
C5—C6—H6	120.0	N—C13—H13A	109.9
C1—C6—H6	120.0	C12—C13—H13A	109.9
O2—C7—C1	121.1 (2)	N—C13—H13B	109.9
O2—C7—C8	119.9 (2)	C12—C13—H13B	109.9
C1—C7—C8	118.8 (2)	H13A—C13—H13B	108.3
C7—C8—C14	108.8 (2)	C8—C14—H14A	109.5
C7—C8—S1	111.58 (17)	C8—C14—H14B	109.5
C14—C8—S1	106.75 (17)	H14A—C14—H14B	109.5
C7—C8—H8	109.9	C8—C14—H14C	109.5
C14—C8—H8	109.9	H14A—C14—H14C	109.5
S1—C8—H8	109.9	H14B—C14—H14C	109.5

C6—C1—C2—O1	178.9 (2)	O2—C7—C8—S1	−25.7 (3)
C7—C1—C2—O1	0.4 (3)	C1—C7—C8—S1	159.95 (17)
C6—C1—C2—C3	−1.8 (3)	C9—S1—C8—C7	−65.12 (19)
C7—C1—C2—C3	179.7 (2)	C9—S1—C8—C14	176.19 (17)
O1—C2—C3—C4	−178.6 (2)	C10—N—C9—S2	178.1 (2)
C1—C2—C3—C4	2.1 (4)	C13—N—C9—S2	5.6 (4)

C2—C3—C4—C5	−0.7 (4)	C10—N—C9—S1	−4.1 (3)
C3—C4—C5—C6	−0.9 (4)	C13—N—C9—S1	−176.5 (2)
C3—C4—C5—Br	178.7 (2)	C8—S1—C9—N	173.43 (19)
C4—C5—C6—C1	1.2 (4)	C8—S1—C9—S2	−8.64 (18)
Br—C5—C6—C1	−178.47 (18)	C9—N—C10—C11	133.4 (3)
C2—C1—C6—C5	0.2 (3)	C13—N—C10—C11	−53.5 (3)
C7—C1—C6—C5	178.6 (2)	C12—O3—C11—C10	−60.2 (3)
C6—C1—C7—O2	−177.6 (2)	N—C10—C11—O3	56.1 (3)
C2—C1—C7—O2	0.8 (3)	C11—O3—C12—C13	61.1 (3)
C6—C1—C7—C8	−3.3 (3)	C9—N—C13—C12	−132.4 (3)
C2—C1—C7—C8	175.1 (2)	C10—N—C13—C12	54.3 (3)
O2—C7—C8—C14	91.8 (3)	O3—C12—C13—N	−57.7 (3)
C1—C7—C8—C14	−82.6 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.76 (4)	1.86 (4)	2.558 (3)	151 (5)
C4—H4···S2^{i}	0.95	2.79	3.712 (3)	164
C3—H3···O3^{ii}	0.95	2.51	3.443 (4)	168
C12—H12*B*···O1^{iii}	0.99	2.46	3.454 (4)	178

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