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2,2′-Bis(methylene)-3,3′-(2-thioxo-2,3-dihydro-1*H*-benzimidazole-1,3-diyl)-dipropanenitrile

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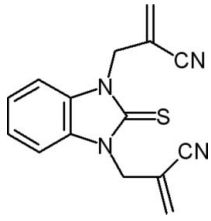
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.039; wR factor = 0.111; data-to-parameter ratio = 18.2.

In the title compound, $C_{15}H_{12}N_4S$, the benzimidazole ring is essentially planar, with a mean deviation of 0.0082 (1) Å from the least-squares plane defined by the nine constituent atoms. In the crystal, inversion dimers linked by pairs of C—H···N hydrogen bonds occur.

Related literature

Benzimidazole is a potential precursor in heterocyclic chemistry and the benzimidazol-2-thione ring is present in many pharmacologically active substances, see: Hwa *et al.* (2008). For ammonium salts from Mannich adducts as precursors for the synthesis of acrylic derivatives carrying functionalized thiomethyl groups, see: M'rabet *et al.* (2009). For a related structure, see: Khan *et al.* (2008). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{15}H_{12}N_4S$ M_r = 280.35
Triclinic, $P\overline{1}$
a = 8.6274 (3) Å
b = 9.8271 (2) Å
c = 9.8271 (2) Å
α = 70.553 (2)°
β = 89.730 (2)°
γ = 67.853 (3)°
V = 720.67 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.22 mm^{-1}
T = 293 K
0.22 × 0.20 × 0.18 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Absorption correction: none
6594 measured reflections
3297 independent reflections
2449 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
2 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.111
S = 1.02
3297 reflections
181 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11B···N4^{i}	0.93	2.51	3.387 (3)	158

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2216).

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supplementary materials

Acta Cryst. (2009). E**65**, o2947 [**doi:10.1107/S1600536809043438**]

2,2'-Bis(methylene)-3,3'-(2-thioxo-2,3-dihydro-1*H*-benzimidazole-1,3-diyl)dipropanenitrile

O. M. Mohamed, H. M'rabet, H. Hemissi and M. El Efrit

Comment

Benzimidazole is an important scaffold in heterocyclic chemistry and benzimidazol-2-thione ring is present in many pharmacologically active substances (Hwa *et al.*, 2008). We recently showed that ammonium salts coming from Mannich adducts, constitute precursors interesting for the synthesis of acrylic derivatives carrying functionalized thiomethyle groups (M'rabet *et al.*, 2009). The results obtained encouraged us to try the action of other functionalized thiols, e.g., mercaptobenzimidazole. The analysis of the spectra for the isolated product shows that the nucleophilic attack utilized the two nitrogen atoms of the mercaptobenzimidazole whatever the stoichiometry was used. The compound was identified unequocally as *N,N*-bis(2-cyanoprop-2-enyl)benzimidazol-2-thione, (I), by the X-ray diffraction analysis.

The bond lengths and angles in the structure of (I) (Fig. 1) are in agreement with the corresponding bond lengths and angles reported for a compound closely related to (I) (Khan, H. *et al.*, 2008) and are within normal ranges (Allen *et al.*, 1987). The benzimidazole ring in (I) is essentially planar with a mean deviation of 0.0028 (1) Å from the least-squares plane defined by the nine constituent atoms. The molecular packing is stabilized by van der Waals interactions and intramolecular (C—H···S) and intermolecular (C—H···N) hydrogen bonds, which link the molecules into dimmers (Table 1 and Fig. 2).

Experimental

To a solution of ammonium salt (12 mmol) in ethanol (50 ml), was added dropwise with stirring 10 mmol of mercaptobenzimidazole. The reaction mixture was stirred for 24 h at room temperature. The residual salt was then filtered and the solvent was removed. The obtained residue was diluted with water (20 ml) and extracted with chloroform. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The product was chromatographed using a silica gel column with 60/40 ether/petroleum ether. The slow evaporation from the solvent afforded crystals of the title compound suitable for X-ray diffraction study.

Refinement

All H atoms were positioned geometrically and treated as riding on the parent atoms [N–H = 0.89, C–H =0.96 Å (CH_3) with U_{iso}(H) = 1.5U_{eq} and C–H = 0.96 Å (Ar–H), with U_{iso}(H) = 1.5U_{eq}].

Figures

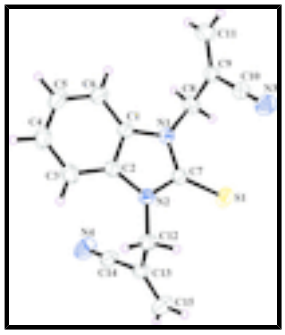

Fig. 1. A perspective view of the molecule of (I) with displacement ellipsoids shown at the 30% probability level.

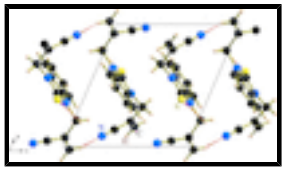

Fig. 2. Molecular packing in the unit cell of (I) showing H-bonding interactions; H-atoms not involved in H-bonds have been excluded.

2,2'-Bis(methylene)-3,3'-(2-thioxo-2,3-dihydro-1*H*-benzimidazole- 1,3-diyl)dipropanenitrile

Crystal data

$C_{15}H_{12}N_4S_1$	$Z = 2$
$M_r = 280.35$	$F_{000} = 292$
Triclinic, $P\overline{1}$	$D_x = 1.292$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.6274$ (3) Å	Cell parameters from 25 reflections
$b = 9.8271$ (2) Å	$\theta = 9.0$–11.0º
$c = 9.8271$ (2) Å	$\mu = 0.22$ mm^{-1}
$\alpha = 70.553$ (2)º	$T = 293$ K
$\beta = 89.730$ (2)º	Prism, colourless
$\gamma = 67.853$ (3)º	0.22 × 0.20 × 0.18 mm
$V = 720.67$ (3) Å^3	

Data collection

Enraf–Nonius TurboCAD-4 diffractometer	$R_{int} = 0.018$
Radiation source: fine-focus sealed tube	$\theta_{max} = 28.0$º
Monochromator: graphite	$\theta_{min} = 2.2$º
$T = 293$ K	$h = -11 \rightarrow 11$
Nonprofiled ω scans	$k = -12 \rightarrow 12$
Absorption correction: none	$l = -12 \rightarrow 12$
6594 measured reflections	2 standard reflections
3297 independent reflections	every 120 min
2449 reflections with $I > 2\sigma(I)$	intensity decay: 3%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.039$	H-atom parameters constrained
$wR(F^2) = 0.111$	$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 0.1378P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.002$
3297 reflections	$\Delta\rho_{max} = 0.19$ e Å^{-3}
181 parameters	$\Delta\rho_{min} = -0.32$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s 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}
S1	0.21056 (7)	0.61386 (6)	0.54777 (5)	0.06747 (18)
N1	0.12971 (16)	0.64019 (15)	0.80813 (13)	0.0438 (3)
N2	0.36099 (16)	0.43553 (15)	0.82525 (13)	0.0443 (3)
C2	0.33686 (19)	0.43018 (18)	0.96681 (16)	0.0429 (3)
C1	0.19084 (19)	0.55980 (18)	0.95584 (16)	0.0421 (3)
C7	0.2340 (2)	0.56319 (18)	0.72744 (16)	0.0452 (3)
C9	0.01720 (18)	0.92638 (18)	0.74111 (16)	0.0447 (3)
C10	0.1474 (2)	0.95298 (19)	0.65727 (17)	0.0478 (4)
C14	0.3569 (2)	0.1382 (2)	0.84115 (19)	0.0529 (4)
C13	0.45594 (19)	0.20653 (18)	0.74643 (17)	0.0455 (3)
C12	0.5016 (2)	0.3244 (2)	0.78361 (19)	0.0510 (4)
H12A	0.5942	0.2689	0.8632	0.061*
H12B	0.5405	0.3823	0.7000	0.061*
N3	0.2515 (2)	0.9733 (2)	0.59254 (18)	0.0649 (4)
C6	0.1282 (2)	0.5886 (2)	1.07808 (18)	0.0529 (4)
H6	0.0298	0.6752	1.0707	0.063*
C8	−0.0187 (2)	0.78626 (19)	0.74714 (19)	0.0510 (4)
H8A	−0.1083	0.7813	0.8060	0.061*
H8B	−0.0575	0.7988	0.6495	0.061*

N4	0.2784 (2)	0.0869 (2)	0.9192 (2)	0.0810 (5)
C3	0.4283 (2)	0.3241 (2)	1.10096 (18)	0.0563 (4)
H3	0.5264	0.2372	1.1085	0.068*
C5	0.2197 (3)	0.4820 (2)	1.21154 (19)	0.0638 (5)
H5	0.1814	0.4969	1.2962	0.077*
C15	0.5064 (3)	0.1615 (3)	0.6360 (2)	0.0681 (5)
H15A	0.4778	0.0855	0.6195	0.082*
H15B	0.5706	0.2057	0.5745	0.082*
C11	−0.0631 (2)	1.0256 (2)	0.8061 (2)	0.0638 (5)
H11A	−0.0353	1.1105	0.7973	0.077*
H11B	−0.1475	1.0105	0.8607	0.077*
C4	0.3670 (3)	0.3534 (2)	1.22258 (19)	0.0651 (5)
H4	0.4260	0.2853	1.3143	0.078*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0965 (4)	0.0682 (3)	0.0385 (2)	−0.0351 (3)	0.0141 (2)	−0.0176 (2)
N1	0.0492 (7)	0.0414 (7)	0.0399 (6)	−0.0177 (5)	0.0080 (5)	−0.0138 (5)
N2	0.0505 (7)	0.0423 (7)	0.0441 (7)	−0.0195 (6)	0.0117 (5)	−0.0193 (5)
C2	0.0511 (8)	0.0414 (8)	0.0432 (7)	−0.0239 (7)	0.0072 (6)	−0.0172 (6)
C1	0.0502 (8)	0.0432 (8)	0.0403 (7)	−0.0250 (7)	0.0090 (6)	−0.0166 (6)
C7	0.0570 (9)	0.0446 (8)	0.0419 (8)	−0.0268 (7)	0.0121 (7)	−0.0173 (6)
C9	0.0394 (7)	0.0421 (8)	0.0441 (8)	−0.0114 (6)	0.0058 (6)	−0.0107 (6)
C10	0.0486 (9)	0.0456 (8)	0.0487 (8)	−0.0170 (7)	0.0085 (7)	−0.0181 (7)
C14	0.0571 (10)	0.0575 (10)	0.0575 (9)	−0.0287 (8)	0.0212 (8)	−0.0303 (8)
C13	0.0442 (8)	0.0462 (8)	0.0505 (8)	−0.0196 (7)	0.0147 (6)	−0.0208 (7)
C12	0.0476 (8)	0.0542 (9)	0.0620 (10)	−0.0240 (7)	0.0193 (7)	−0.0295 (8)
N3	0.0637 (9)	0.0732 (11)	0.0700 (10)	−0.0339 (8)	0.0260 (8)	−0.0331 (8)
C6	0.0649 (10)	0.0564 (10)	0.0522 (9)	−0.0317 (8)	0.0190 (8)	−0.0287 (8)
C8	0.0446 (8)	0.0502 (9)	0.0538 (9)	−0.0182 (7)	0.0051 (7)	−0.0142 (7)
N4	0.0919 (13)	0.1025 (14)	0.0810 (12)	−0.0640 (12)	0.0448 (10)	−0.0434 (11)
C3	0.0618 (10)	0.0496 (9)	0.0524 (9)	−0.0208 (8)	−0.0045 (8)	−0.0136 (8)
C5	0.0945 (14)	0.0776 (13)	0.0429 (9)	−0.0515 (12)	0.0189 (9)	−0.0303 (9)
C15	0.0859 (13)	0.0850 (14)	0.0663 (11)	−0.0532 (12)	0.0376 (10)	−0.0450 (11)
C11	0.0618 (11)	0.0577 (11)	0.0732 (12)	−0.0217 (9)	0.0246 (9)	−0.0272 (9)
C4	0.0887 (14)	0.0639 (11)	0.0425 (9)	−0.0355 (11)	−0.0051 (9)	−0.0125 (8)

Geometric parameters (Å, °)

S1—C7	1.6577 (15)	C9—C11	1.319 (3)
N1—C1	1.3924 (19)	C12—C13	1.503 (3)
N1—C7	1.375 (2)	C13—C14	1.434 (2)
N1—C8	1.452 (2)	C13—C15	1.317 (3)
N2—C2	1.3922 (19)	C3—H3	0.9300
N2—C7	1.367 (2)	C4—H4	0.9300
N2—C12	1.458 (2)	C5—H5	0.9300
N3—C10	1.138 (3)	C6—H6	0.9300
N4—C14	1.139 (3)	C8—H8A	0.9700

C1—C2	1.386 (2)	C8—H8B	0.9700
C1—C6	1.386 (2)	C11—H11A	0.9300
C2—C3	1.386 (2)	C11—H11B	0.9300
C3—C4	1.378 (3)	C12—H12A	0.9700
C4—C5	1.387 (4)	C12—H12B	0.9700
C5—C6	1.383 (3)	C15—H15A	0.9300
C8—C9	1.504 (3)	C15—H15B	0.9300
C9—C10	1.442 (2)		
C1—N1—C7	109.85 (14)	C14—C13—C15	119.89 (19)
C1—N1—C8	125.42 (14)	N4—C14—C13	177.6 (2)
C7—N1—C8	124.70 (13)	C2—C3—H3	122.00
C2—N2—C7	110.30 (14)	C4—C3—H3	122.00
C2—N2—C12	126.00 (14)	C3—C4—H4	119.00
C7—N2—C12	123.70 (13)	C5—C4—H4	119.00
N1—C1—C2	106.98 (14)	C4—C5—H5	119.00
N1—C1—C6	131.26 (16)	C6—C5—H5	119.00
C2—C1—C6	121.74 (15)	C1—C6—H6	122.00
N2—C2—C1	106.69 (13)	C5—C6—H6	122.00
N2—C2—C3	131.89 (16)	N1—C8—H8A	109.00
C1—C2—C3	121.42 (15)	N1—C8—H8B	109.00
C2—C3—C4	116.90 (18)	C9—C8—H8A	109.00
C3—C4—C5	121.62 (17)	C9—C8—H8B	109.00
C4—C5—C6	121.78 (19)	H8A—C8—H8B	108.00
C1—C6—C5	116.53 (19)	C9—C11—H11A	120.00
S1—C7—N1	127.09 (13)	C9—C11—H11B	120.00
S1—C7—N2	126.73 (13)	H11A—C11—H11B	120.00
N1—C7—N2	106.18 (12)	N2—C12—H12A	109.00
N1—C8—C9	111.91 (15)	N2—C12—H12B	109.00
C8—C9—C10	117.04 (15)	C13—C12—H12A	109.00
C8—C9—C11	124.34 (16)	C13—C12—H12B	109.00
C10—C9—C11	118.62 (16)	H12A—C12—H12B	108.00
N3—C10—C9	179.21 (18)	C13—C15—H15A	120.00
N2—C12—C13	113.07 (15)	C13—C15—H15B	120.00
C12—C13—C14	116.74 (15)	H15A—C15—H15B	120.00
C12—C13—C15	123.33 (19)		
C7—N1—C1—C2	0.2 (2)	C2—N2—C12—C13	101.76 (19)
C7—N1—C1—C6	−178.16 (19)	C7—N2—C12—C13	−79.4 (2)
C8—N1—C1—C2	−177.94 (16)	N1—C1—C2—N2	0.21 (19)
C8—N1—C1—C6	3.7 (3)	N1—C1—C2—C3	−179.34 (16)
C1—N1—C7—S1	179.15 (14)	C6—C1—C2—N2	178.77 (16)
C1—N1—C7—N2	−0.56 (19)	C6—C1—C2—C3	−0.8 (3)
C8—N1—C7—S1	−2.7 (3)	N1—C1—C6—C5	178.7 (2)
C8—N1—C7—N2	177.61 (15)	C2—C1—C6—C5	0.5 (3)
C1—N1—C8—C9	78.8 (2)	N2—C2—C3—C4	−179.3 (2)
C7—N1—C8—C9	−99.06 (19)	C1—C2—C3—C4	0.2 (3)
C7—N2—C2—C1	−0.6 (2)	C2—C3—C4—C5	0.7 (3)
C7—N2—C2—C3	178.92 (19)	C3—C4—C5—C6	−1.0 (4)
C12—N2—C2—C1	178.44 (16)	C4—C5—C6—C1	0.3 (4)

C12—N2—C2—C3	−2.1 (3)	N1—C8—C9—C10	59.16 (19)
C2—N2—C7—S1	−179.02 (14)	N1—C8—C9—C11	−121.4 (2)
C2—N2—C7—N1	0.69 (19)	N2—C12—C13—C14	−43.4 (2)
C12—N2—C7—S1	2.0 (3)	N2—C12—C13—C15	138.7 (2)
C12—N2—C7—N1	−178.34 (15)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8B···S1	0.97	2.77	3.204 (2)	108
C11—H11B···N4^{i}	0.93	2.51	3.387 (3)	158

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

Fig. 1

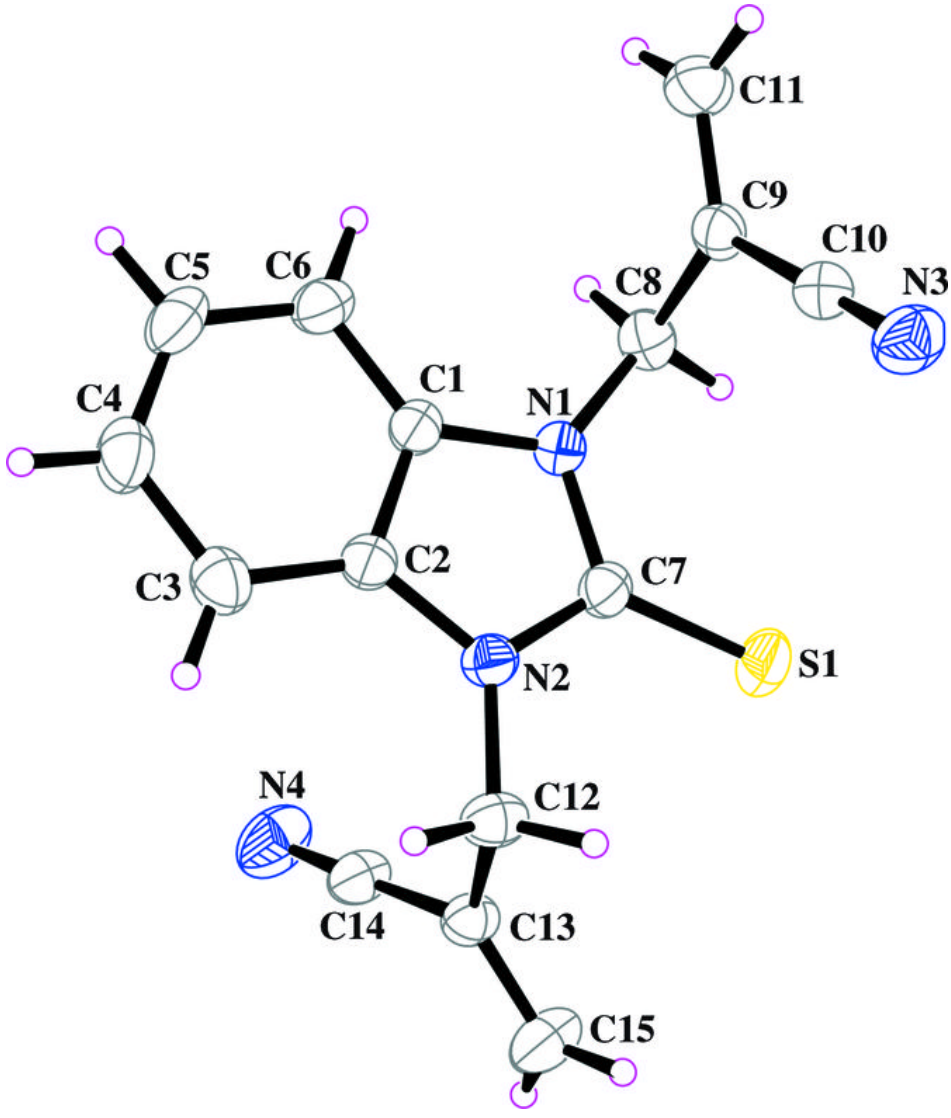

Fig. 2