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2,2'-(Sulfanediyl)dimethylenebis(1,3-benzothiazole)

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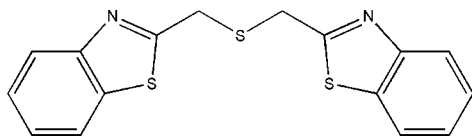
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å;
 R factor = 0.035; wR factor = 0.088; data-to-parameter ratio = 15.5.

In the title compound, $\text{C}_{16}\text{H}_{12}\text{N}_2\text{S}_3$, the two benzothiazole groups are oriented differently with respect to the $-\text{CH}_2-$ groups, one being approximately staggered and one nearly eclipsed. A sulfur– π interaction of 3.3627 (11) Å is observed between the bridging thioether S atom and a thiazole ring. The crystal packing is further stabilized by intermolecular C–H \cdots N and C–H $\cdots\pi$ interactions.

Related literature

For the preparation of the title compound, see: Rai & Braunwarth (1961). For a related structure, see: Clegg & Elsegood (2005). For S $\cdots\pi$ interactions, see: Singh *et al.* (2006).



Experimental

Crystal data

$\text{C}_{16}\text{H}_{12}\text{N}_2\text{S}_3$
 $M_r = 328.46$
Triclinic, $P\bar{1}$
 $a = 6.3714$ (10) Å
 $b = 7.8748$ (13) Å
 $c = 15.339$ (3) Å
 $\alpha = 78.616$ (3)°
 $\beta = 89.537$ (3)°

$\gamma = 74.707$ (3)°
 $V = 727.0$ (2) Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.50$ mm⁻¹
 $T = 100$ K
0.15 × 0.13 × 0.13 mm

Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\min} = 0.809$, $T_{\max} = 0.938$
8237 measured reflections
2942 independent reflections
2584 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.088$
 $S = 1.05$
2942 reflections
190 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.37$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C3–C8 ring.

D–H \cdots A	D–H	H \cdots A	D \cdots A	D–H \cdots A
C1–H1B \cdots N1 ⁱ	0.99	2.57	3.519 (3)	161
C13–H13 \cdots N2 ⁱⁱ	0.95	2.61	3.441 (3)	146
C1–H1A \cdots Cg1 ⁱⁱⁱ	0.99	2.75	3.650 (2)	?
C9–H9A \cdots Cg1 ^{iv}	0.99	2.84	3.610 (3)	?

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x-1, y, z$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+2, -y, -z+1$.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: X-SEED (Barbour, 2001; Atwood & Barbour, 2003); software used to prepare material for publication: X-SEED and PLATON (Spek, 2009).

We would like to thank the National Research Foundation (NRF) of South Africa for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZQ2087).

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supporting information

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2,2'-(Sulfanediyl dimethylene)bis(1,3-benzothiazole)

Christoph E. Strasser, Leigh-Anne de Jongh, Helgard G. Raubenheimer and Stephanie Cronje

S1. Comment

Within the benzothiazole rings of the title compound (Fig. 1) no differences are observed in bond lengths and angles. In the bridge, however, the values for the two S—C—C angles [107.72 (13)° and 113.74 (14)°] and S—C bonds [1.823 (2) and 1.803 (2) Å] differ significantly. This deviation may be explained with the two different S3—C—C—S torsion angles of 71.44 (17) and 27.1 (2)° of the respective benzothiazolyl moieties.

A related structure where one benzothiazole and one benzimidazole moiety is present was determined by Clegg & Elsegood (2005). The arrangement of the molecule in this structure is similar to the one determined here, albeit the orientation of the heterocycles with respect to the CH₂ groups is more uniform [values for the S1—C9—C10—N3(H) and S1—C1—C2—S2 torsion angles -90.6 (7)° and -69.4 (6)°, respectively].

Interactions between neighbouring molecules in the title compound are summarized in Table 1. They include two unique C—H...N contacts between H1B and N1ⁱ [symmetry code (i) $-x + 2, -y + 1, -z + 1$] as well as between H13 and N2ⁱⁱ [symmetry code (ii) $x - 1, y, z$], leading to columns of associated molecules running parallel to the crystallographic *a* axis. The hydrogen atoms H1A and H9A of the CH₂ groups are furthermore engaged in C—H... π interactions with benzo groups at distances of 2.75 Å [H1A...Cg1ⁱⁱⁱ, (iii) $-x + 1, -y + 1, -z + 1$] and 2.84 Å [H9A...Cg1^{iv}, (iv) $-x + 2, -y, -z + 1$] [C1...Cg1ⁱⁱⁱ 3.650 (2) Å, C9...Cg1^{iv} 3.610 (3) Å].

An offset parallel thiazole ring stacking [centroid distance Cg2...Cg2ⁱⁱⁱ 3.6724 (12) Å] of the rings containing S1 related by a centre of inversion is also found. Finally, a S... π interaction is observed between S3 and the thiazole ring containing S1, the S3...Cg2^{iv} distance is 3.3627 (11) Å which is shorter than the thione S... π interaction (3.631 Å) found in the solid state of 5-(2-chloroethyl)-6-methyl-2-thiouracil (Singh *et al.*, 2006).

S2. Experimental

The compound was synthesized from 2,2'-thiodiethanoic acid and *o*-aminothiophenol as described in the literature procedure for the preparation of 2,2'-[thiobis(ethylene)]bis(benzo-1,3-thiazole) (Rai & Braunwarth, 1961).

NMR (CD₂Cl₂): ¹H (400 MHz): δ 7.95 (m, 2 H), 7.87 (m, 2 H), 7.47 (m, 2 H), 7.38 (m, 2 H), 4.24 (s, 4 H, CH₂) p.p.m.; ¹³C {¹H} (101 MHz): δ 169.0, 153.8, 136.4, 126.6, 125.7, 123.5, 122.2, 34.4 p.p.m.

MS (ESI): *m/z* (intensity) 332.0331 (2%, C₁₅¹³CH₁₃N₂S₂³⁴S⁺ calcd. 332.0227), 331.0282 (15, C₁₆H₁₃N₂S₂³⁴S⁺ calcd. 331.0193), 330.0335 (18, C₁₅¹³CH₁₃N₂S₃⁺ calcd. 330.0270), 329.0242 (100, C₁₆H₁₃N₂S₃⁺ calcd. 329.0235), 295.0449 (4, C₁₆H₁₁N₂S₂⁺ calcd. 295.0358).

S3. Refinement

All H atoms were positioned geometrically (C—H = 0.95 Å for aromatic CH and 0.99 Å for CH₂ groups, respectively) and constrained to ride on their parent atoms with *U*_{iso}(H) values set at 1.2 times *U*_{eq}(C).

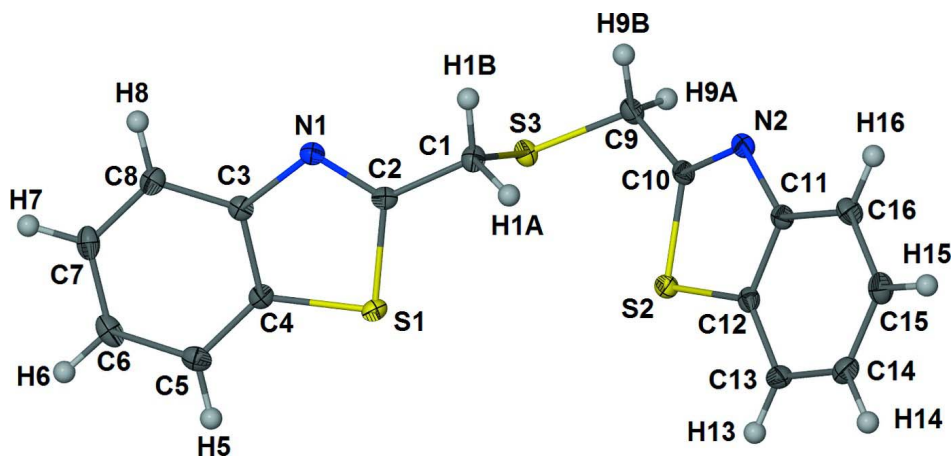


Figure 1

The asymmetric unit of the title compound. Ellipsoids are drawn at the 50% probability level.

2,2'-(Sulfanediyl)dimethylenebis(1,3-benzothiazole)

Crystal data

$C_{16}H_{12}N_2S_3$

$M_r = 328.46$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 6.3714$ (10) Å

$b = 7.8748$ (13) Å

$c = 15.339$ (3) Å

$\alpha = 78.616$ (3)°

$\beta = 89.537$ (3)°

$\gamma = 74.707$ (3)°

$V = 727.0$ (2) Å³

$Z = 2$

$F(000) = 340$

$D_x = 1.500$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2489 reflections

$\theta = 2.7$ – 26.3 °

$\mu = 0.50$ mm⁻¹

$T = 100$ K

Prism, colourless

$0.15 \times 0.13 \times 0.13$ mm

Data collection

Bruker APEX CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2002)

$T_{\min} = 0.809$, $T_{\max} = 0.938$

8237 measured reflections

2942 independent reflections

2584 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 26.4$ °, $\theta_{\min} = 2.7$ °

$h = -7 \rightarrow 7$

$k = -9 \rightarrow 9$

$l = -19 \rightarrow 19$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.088$

$S = 1.05$

2942 reflections

190 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-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 0.3246P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.37$ e Å⁻³

$\Delta\rho_{\min} = -0.21$ e Å⁻³

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.53975 (8)	0.21565 (6)	0.51882 (3)	0.01656 (13)
N1	0.7847 (3)	0.3908 (2)	0.42435 (10)	0.0151 (3)
C1	0.9069 (3)	0.2967 (3)	0.58191 (13)	0.0172 (4)
H1A	0.8209	0.3306	0.6328	0.021*
H1B	1.0025	0.3779	0.5661	0.021*
S2	0.82962 (8)	0.06186 (7)	0.79611 (3)	0.01754 (14)
N2	1.1321 (3)	0.1947 (2)	0.84450 (11)	0.0168 (4)
C2	0.7589 (3)	0.3120 (2)	0.50442 (13)	0.0146 (4)
S3	1.07030 (8)	0.06391 (6)	0.61145 (3)	0.01686 (13)
C3	0.6238 (3)	0.3805 (2)	0.36660 (13)	0.0154 (4)
C4	0.4736 (3)	0.2891 (2)	0.40572 (12)	0.0155 (4)
C5	0.3029 (3)	0.2694 (3)	0.35627 (14)	0.0192 (4)
H5	0.2021	0.2076	0.3834	0.023*
C6	0.2851 (3)	0.3430 (3)	0.26593 (14)	0.0222 (5)
H6	0.1697	0.3317	0.2306	0.027*
C7	0.4337 (3)	0.4336 (3)	0.22579 (13)	0.0207 (4)
H7	0.4178	0.4823	0.1637	0.025*
C8	0.6032 (3)	0.4535 (3)	0.27507 (13)	0.0190 (4)
H8	0.7035	0.5153	0.2475	0.023*
C9	1.2192 (3)	0.0752 (3)	0.70864 (13)	0.0189 (4)
H9A	1.3282	-0.0417	0.7291	0.023*
H9B	1.2992	0.1681	0.6919	0.023*
C10	1.0779 (3)	0.1183 (3)	0.78436 (12)	0.0161 (4)
C11	0.9748 (3)	0.2116 (3)	0.90792 (13)	0.0163 (4)
C12	0.7962 (3)	0.1475 (3)	0.89280 (12)	0.0160 (4)
C13	0.6216 (3)	0.1623 (3)	0.94854 (13)	0.0197 (4)
H13	0.4992	0.1214	0.9367	0.024*
C14	0.6321 (3)	0.2384 (3)	1.02160 (13)	0.0212 (4)
H14	0.5158	0.2489	1.0610	0.025*
C15	0.8112 (3)	0.3003 (3)	1.03843 (13)	0.0218 (4)
H15	0.8152	0.3514	1.0893	0.026*
C16	0.9823 (3)	0.2883 (3)	0.98216 (13)	0.0201 (4)
H16	1.1031	0.3314	0.9937	0.024*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0170 (3)	0.0169 (3)	0.0167 (2)	-0.0062 (2)	0.00418 (18)	-0.00351 (19)
N1	0.0156 (8)	0.0127 (8)	0.0178 (8)	-0.0045 (7)	0.0012 (6)	-0.0040 (6)
C1	0.0226 (10)	0.0131 (9)	0.0165 (10)	-0.0057 (8)	-0.0003 (8)	-0.0034 (8)
S2	0.0194 (3)	0.0194 (3)	0.0163 (2)	-0.0091 (2)	-0.00021 (19)	-0.00424 (19)
N2	0.0154 (8)	0.0172 (8)	0.0172 (8)	-0.0037 (7)	-0.0014 (6)	-0.0029 (7)
C2	0.0154 (9)	0.0108 (9)	0.0188 (10)	-0.0038 (8)	0.0024 (7)	-0.0058 (7)
S3	0.0175 (3)	0.0159 (3)	0.0170 (3)	-0.00225 (19)	-0.00110 (19)	-0.00597 (19)
C3	0.0156 (10)	0.0105 (9)	0.0190 (10)	-0.0010 (8)	0.0006 (8)	-0.0042 (7)
C4	0.0157 (10)	0.0129 (9)	0.0170 (9)	-0.0016 (8)	0.0025 (7)	-0.0042 (8)
C5	0.0143 (10)	0.0152 (10)	0.0271 (11)	-0.0013 (8)	0.0010 (8)	-0.0053 (8)
C6	0.0218 (11)	0.0158 (10)	0.0278 (11)	0.0002 (8)	-0.0069 (9)	-0.0084 (9)
C7	0.0260 (11)	0.0144 (10)	0.0181 (10)	0.0009 (8)	-0.0047 (8)	-0.0027 (8)
C8	0.0229 (11)	0.0151 (10)	0.0180 (10)	-0.0040 (8)	0.0023 (8)	-0.0029 (8)
C9	0.0158 (10)	0.0230 (11)	0.0177 (10)	-0.0032 (8)	-0.0012 (8)	-0.0065 (8)
C10	0.0156 (10)	0.0139 (9)	0.0169 (10)	-0.0029 (8)	-0.0029 (8)	0.0001 (8)
C11	0.0158 (10)	0.0130 (9)	0.0177 (10)	-0.0023 (8)	-0.0022 (8)	0.0007 (8)
C12	0.0195 (10)	0.0129 (9)	0.0150 (9)	-0.0051 (8)	-0.0022 (8)	-0.0003 (7)
C13	0.0191 (10)	0.0201 (10)	0.0197 (10)	-0.0086 (8)	0.0006 (8)	0.0006 (8)
C14	0.0211 (11)	0.0219 (11)	0.0187 (10)	-0.0042 (9)	0.0039 (8)	-0.0016 (8)
C15	0.0250 (11)	0.0212 (11)	0.0184 (10)	-0.0030 (9)	-0.0013 (8)	-0.0067 (8)
C16	0.0205 (10)	0.0192 (10)	0.0219 (10)	-0.0061 (9)	-0.0024 (8)	-0.0064 (8)

Geometric parameters (Å, °)

S1—C4	1.7346 (19)	C6—C7	1.399 (3)
S1—C2	1.7503 (19)	C6—H6	0.9500
N1—C2	1.292 (2)	C7—C8	1.383 (3)
N1—C3	1.389 (2)	C7—H7	0.9500
C1—C2	1.489 (3)	C8—H8	0.9500
C1—S3	1.823 (2)	C9—C10	1.501 (3)
C1—H1A	0.9900	C9—H9A	0.9900
C1—H1B	0.9900	C9—H9B	0.9900
S2—C12	1.736 (2)	C11—C16	1.397 (3)
S2—C10	1.751 (2)	C11—C12	1.399 (3)
N2—C10	1.291 (3)	C12—C13	1.392 (3)
N2—C11	1.390 (2)	C13—C14	1.381 (3)
S3—C9	1.803 (2)	C13—H13	0.9500
C3—C8	1.401 (3)	C14—C15	1.398 (3)
C3—C4	1.406 (3)	C14—H14	0.9500
C4—C5	1.390 (3)	C15—C16	1.380 (3)
C5—C6	1.386 (3)	C15—H15	0.9500
C5—H5	0.9500	C16—H16	0.9500
C4—S1—C2	88.91 (9)	C7—C8—H8	120.7
C2—N1—C3	110.15 (16)	C3—C8—H8	120.7

C2—C1—S3	107.72 (13)	C10—C9—S3	113.74 (14)
C2—C1—H1A	110.2	C10—C9—H9A	108.8
S3—C1—H1A	110.2	S3—C9—H9A	108.8
C2—C1—H1B	110.2	C10—C9—H9B	108.8
S3—C1—H1B	110.2	S3—C9—H9B	108.8
H1A—C1—H1B	108.5	H9A—C9—H9B	107.7
C12—S2—C10	88.55 (9)	N2—C10—C9	122.79 (18)
C10—N2—C11	110.20 (17)	N2—C10—S2	116.52 (15)
N1—C2—C1	123.58 (17)	C9—C10—S2	120.68 (15)
N1—C2—S1	116.45 (15)	N2—C11—C16	125.20 (18)
C1—C2—S1	119.96 (14)	N2—C11—C12	115.28 (17)
C9—S3—C1	99.65 (9)	C16—C11—C12	119.52 (18)
N1—C3—C8	124.87 (17)	C13—C12—C11	121.76 (18)
N1—C3—C4	115.51 (17)	C13—C12—S2	128.76 (16)
C8—C3—C4	119.62 (18)	C11—C12—S2	109.43 (14)
C5—C4—C3	121.90 (18)	C14—C13—C12	117.83 (19)
C5—C4—S1	129.11 (15)	C14—C13—H13	121.1
C3—C4—S1	108.99 (14)	C12—C13—H13	121.1
C6—C5—C4	117.59 (18)	C13—C14—C15	121.05 (19)
C6—C5—H5	121.2	C13—C14—H14	119.5
C4—C5—H5	121.2	C15—C14—H14	119.5
C5—C6—C7	121.29 (19)	C16—C15—C14	120.97 (19)
C5—C6—H6	119.4	C16—C15—H15	119.5
C7—C6—H6	119.4	C14—C15—H15	119.5
C8—C7—C6	121.10 (19)	C15—C16—C11	118.84 (19)
C8—C7—H7	119.5	C15—C16—H16	120.6
C6—C7—H7	119.5	C11—C16—H16	120.6
C7—C8—C3	118.51 (18)		
C3—N1—C2—C1	178.89 (17)	C1—S3—C9—C10	64.24 (16)
C3—N1—C2—S1	0.4 (2)	C11—N2—C10—C9	-177.69 (17)
S3—C1—C2—N1	-106.97 (19)	C11—N2—C10—S2	1.1 (2)
S3—C1—C2—S1	71.44 (17)	S3—C9—C10—N2	-154.18 (16)
C4—S1—C2—N1	-0.29 (16)	S3—C9—C10—S2	27.1 (2)
C4—S1—C2—C1	-178.80 (16)	C12—S2—C10—N2	-0.75 (16)
C2—C1—S3—C9	-176.45 (13)	C12—S2—C10—C9	178.10 (16)
C2—N1—C3—C8	179.46 (18)	C10—N2—C11—C16	179.98 (19)
C2—N1—C3—C4	-0.4 (2)	C10—N2—C11—C12	-1.0 (2)
N1—C3—C4—C5	179.49 (17)	N2—C11—C12—C13	-177.23 (17)
C8—C3—C4—C5	-0.4 (3)	C16—C11—C12—C13	1.8 (3)
N1—C3—C4—S1	0.2 (2)	N2—C11—C12—S2	0.5 (2)
C8—C3—C4—S1	-179.68 (15)	C16—C11—C12—S2	179.54 (15)
C2—S1—C4—C5	-179.21 (19)	C10—S2—C12—C13	177.61 (19)
C2—S1—C4—C3	0.05 (14)	C10—S2—C12—C11	0.12 (14)
C3—C4—C5—C6	0.2 (3)	C11—C12—C13—C14	-1.8 (3)
S1—C4—C5—C6	179.35 (15)	S2—C12—C13—C14	-179.05 (16)
C4—C5—C6—C7	0.1 (3)	C12—C13—C14—C15	0.7 (3)
C5—C6—C7—C8	-0.3 (3)	C13—C14—C15—C16	0.4 (3)

C6—C7—C8—C3	0.1 (3)	C14—C15—C16—C11	-0.5 (3)
N1—C3—C8—C7	-179.63 (17)	N2—C11—C16—C15	178.31 (18)
C4—C3—C8—C7	0.2 (3)	C12—C11—C16—C15	-0.7 (3)

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the C3—C8 ring.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C1—H1B...N1 ⁱ	0.99	2.57	3.519 (3)	161
C13—H13...N2 ⁱⁱ	0.95	2.61	3.441 (3)	146
C1—H1A...Cg1 ⁱⁱⁱ	0.99	2.75	3.650 (2)	?
C9—H9A...Cg1 ^{iv}	0.99	2.84	3.610 (3)	?

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x-1, y, z$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+2, -y, -z+1$.