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# Crystal structure of 1,5-diethyl-1*H*-1,5-benzodiazepine-2,4(3*H*,5*H*)-dithione

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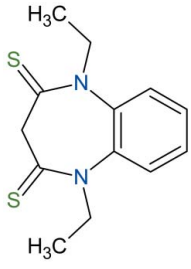
In the title compound, $C_{13}H_{16}N_2S_2$, the seven-membered ring adopts a boat conformation, with the two phenylene C atoms representing the stern and the methylene C atom as the prow. The thione S atoms and N-bound ethyl groups lie on the opposite side of the molecule to the phenylene ring so that the molecule approximates mirror symmetry. In the crystal, supramolecular layers in the *bc* plane are sustained by a pair of C—H···S interactions to the same S atom acceptor.

**Keywords:** crystal structure; benzodiazepine; boat conformation..

**CCDC reference**: 1040593

## 1. Related literature

For the biological activity of benzodiazepine derivatives, see: Kumar *et al.* (2006); Swamy *et al.* (2008). For a related structure, see: Ourahou *et al.* (2010).




## 2. Experimental

### 2.1. Crystal data

$C_{13}H_{16}N_2S_2$
$M_r$ = 264.40
Monoclinic, $C2/c$
$a$ = 19.8896 (2) Å
$b$ = 8.8743 (1) Å
$c$ = 15.5361 (2) Å
$\beta$ = 104.087 (1)°
$V$ = 2659.75 (5) Å$^3$
$Z$ = 8
Mo $K\alpha$ radiation
$\mu$ = 0.38 mm$^{-1}$
$T$ = 150 K
0.44 × 0.28 × 0.26 mm

### 2.2. Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min}$ = 0.880, $T_{max}$ = 0.906
14634 measured reflections
3312 independent reflections
2963 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.022

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.083
$S$ = 1.05
3312 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.39 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.21 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C3—H3···S1$^{i}$ | 0.95 | 2.86 | 3.6474 (13) | 141 |
| C12—H12$A$···S1$^{ii}$ | 0.99 | 2.87 | 3.4887 (13) | 121 |

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT-Plus* (Bruker, 2009); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supporting information for this paper is available from the IUCr electronic archives (Reference: TK5353).

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# supporting information

*Acta Cryst.* (2015). E**71**, o83 [doi:10.1107/S205698901402790X]

## Crystal structure of 1,5-diethyl-1*H*-1,5-benzodiazepine-2,4(3*H*,5*H*)-dithione

**Abderrahman Lamkaddem, Mohamed Harcharras, Abdelillah Shaim, Hafid Zouihri, Bousselham Echchahed and Wenhua Bi**

### S1. Introduction

Benzodiazepines and their derivatives are an important class of bioactive compound. They have attracted attention of chemists in the field of pharmaceuticals (Kumar *et al.*, 2006). Some benzodiazepine derivatives have been widely used as anti-bacterial, anti-fungal, analgesic and anti-convulsant agents (Swamy *et al.* 2008).

### S2. Synthesis and crystallization

In a round flask, the 1,5 dietthyl benzodiazepine-2,4-diones (2,22 g, 10 ml) and $P_2S_5$ (4.44 g, 20 ml) were mixed in aceto-nitrile (50 ml). The mixture was refluxed for 4 h. After this time, the solvent was evaporated, and the residue formed was washed with HCl (2 N) solution and distilled water, dried and recrystallised from toluene-chloroform (90/10). After some days, pale-yellow crystals were isolated (yield: 92.1 %, 2.34 g).

### S3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H-atoms were placed in calculated positions (C—H 0.95–0.99 Å) and were included in the refinement in the riding model approximation, with $U_{iso}$(H) = 1.5$U_{eq}$(C) for methyl H atoms and 1.2$U_{eq}$(C) for all other H atoms.

### S4. Results and discussion

The title compound crystallizes in the space group C2/c with one independent molecule in the asymmetric unit (Fig. 1). In the molecule, the diazepine ring system adopts a boat conformation with the two C1 and C6 atoms representing the stern and the C8 atom the prow with maximum deviation of 0.6626 (12)Å. The puckering parameters are: q2=0.9557 (11) Å, q3 = 0.2328 (11) Å, $\varphi$2 = 29.60 (7)° and $\varphi$3 = 128.4 (3)°. The mean plane of the diazepine ring is twisted with respect to that of the benzene ring by 32.27 (5)°. The geometric parameters of the title compound are comparable to those reported for similar structures (Ourahou *et al.*, 2010).

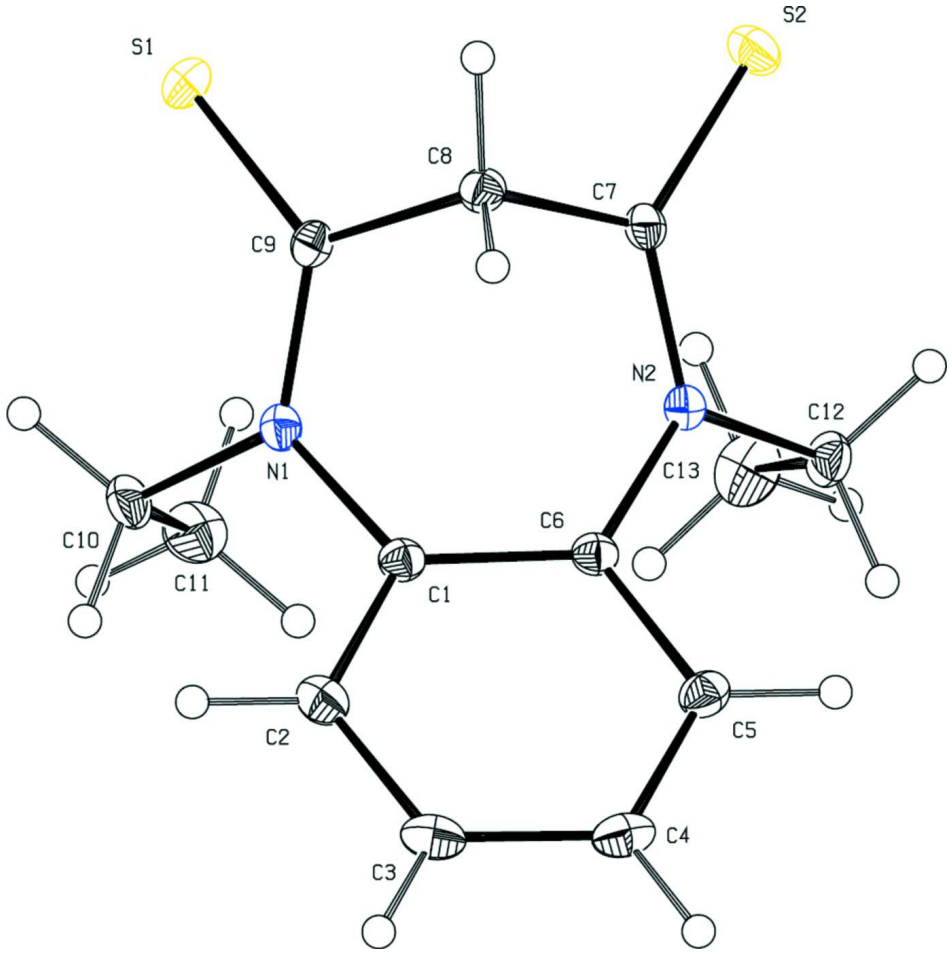


**Figure 1**

The structure of the title compound, showing atom labelling and 30% probability displacement ellipsoids.

### 1,5-Diethyl-1*H*-1,5-benzodiazepine-2,4(3*H*,5*H*)-dithione

*Crystal data*

$C_{13}H_{16}N_2S_2$
$M_r$ = 264.40
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
*a* = 19.8896 (2) Å
*b* = 8.8743 (1) Å
*c* = 15.5361 (2) Å
*β* = 104.087 (1)°
*V* = 2659.75 (5) Å$^3$
*Z* = 8
*F*(000) = 1120
$D_x$ = 1.321 Mg m$^{-3}$
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 7669 reflections
*θ* = 2.5–28.3°
*μ* = 0.38 mm$^{-1}$
*T* = 150 K
Block, pale-yellow
0.44 × 0.28 × 0.26 mm

*Data collection*

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
*φ* and *ω* scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min}$ = 0.880, $T_{max}$ = 0.906
14634 measured reflections
3312 independent reflections

2963 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 28.3°$, $\theta_{min} = 2.1°$
$h = -26 \rightarrow 26$
$k = -11 \rightarrow 9$
$l = -20 \rightarrow 20$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.083$
$S = 1.05$
3312 reflections
154 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
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 1.6941P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.39$ 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 $F^2 > \sigma(F^2)$ 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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.389586 (17) | 0.69948 (4) | 0.221477 (18) | 0.02667 (9) |
| S2 | 0.401294 (17) | 0.32244 (3) | 0.37615 (2) | 0.02698 (9) |
| N1 | 0.38266 (5) | 0.81930 (10) | 0.37619 (6) | 0.01868 (19) |
| N2 | 0.38030 (5) | 0.54640 (10) | 0.48109 (6) | 0.01790 (19) |
| C1 | 0.39904 (5) | 0.82159 (12) | 0.47124 (7) | 0.0180 (2) |
| C2 | 0.41810 (6) | 0.95882 (13) | 0.51444 (8) | 0.0236 (2) |
| H2 | 0.4222 | 1.0462 | 0.4808 | 0.028* |
| C3 | 0.43116 (6) | 0.96826 (15) | 0.60624 (8) | 0.0270 (3) |
| H3 | 0.4443 | 1.0618 | 0.6353 | 0.032* |
| C4 | 0.42499 (6) | 0.84098 (15) | 0.65542 (8) | 0.0258 (3) |
| H4 | 0.4323 | 0.8482 | 0.7180 | 0.031* |
| C5 | 0.40829 (6) | 0.70361 (14) | 0.61388 (7) | 0.0217 (2) |
| H5 | 0.4055 | 0.6164 | 0.6483 | 0.026* |
| C6 | 0.39547 (5) | 0.69179 (12) | 0.52125 (7) | 0.0176 (2) |
| C7 | 0.41267 (5) | 0.49358 (12) | 0.42024 (7) | 0.0183 (2) |
| C8 | 0.45893 (6) | 0.60552 (13) | 0.38859 (7) | 0.0196 (2) |
| H8A | 0.4898 | 0.6575 | 0.4396 | 0.024* |
| H8B | 0.4878 | 0.5541 | 0.3539 | 0.024* |
| C9 | 0.41007 (5) | 0.71650 (12) | 0.33112 (7) | 0.0185 (2) |
| C10 | 0.32917 (6) | 0.92648 (13) | 0.32921 (8) | 0.0255 (2) |
| H10A | 0.3380 | 0.9521 | 0.2709 | 0.031* |
| H10B | 0.3320 | 1.0205 | 0.3642 | 0.031* |

| | | | | |
|---|---|---|---|---|
| C11 | 0.25747 (7) | 0.85946 (17) | 0.31559 (9) | 0.0341 (3) |
| H11A | 0.2230 | 0.9323 | 0.2846 | 0.051* |
| H11B | 0.2485 | 0.8353 | 0.3733 | 0.051* |
| H11C | 0.2544 | 0.7673 | 0.2801 | 0.051* |
| C12 | 0.32830 (6) | 0.45201 (14) | 0.50965 (8) | 0.0245 (2) |
| H12A | 0.3262 | 0.4814 | 0.5704 | 0.029* |
| H12B | 0.3427 | 0.3450 | 0.5112 | 0.029* |
| C13 | 0.25706 (7) | 0.46914 (18) | 0.44750 (10) | 0.0374 (3) |
| H13A | 0.2239 | 0.4054 | 0.4681 | 0.056* |
| H13B | 0.2588 | 0.4385 | 0.3875 | 0.056* |
| H13C | 0.2424 | 0.5746 | 0.4467 | 0.056* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.03626 (18) | 0.02858 (17) | 0.01620 (14) | 0.00172 (12) | 0.00835 (11) | 0.00226 (10) |
| S2 | 0.03522 (18) | 0.01756 (15) | 0.02775 (16) | 0.00255 (11) | 0.00685 (12) | −0.00303 (10) |
| N1 | 0.0206 (4) | 0.0171 (5) | 0.0179 (4) | 0.0015 (3) | 0.0039 (3) | 0.0023 (3) |
| N2 | 0.0195 (4) | 0.0165 (4) | 0.0182 (4) | 0.0003 (3) | 0.0055 (3) | 0.0014 (3) |
| C1 | 0.0159 (5) | 0.0196 (5) | 0.0186 (5) | 0.0016 (4) | 0.0044 (4) | −0.0005 (4) |
| C2 | 0.0233 (5) | 0.0197 (5) | 0.0279 (6) | −0.0003 (4) | 0.0064 (4) | −0.0024 (4) |
| C3 | 0.0249 (6) | 0.0270 (6) | 0.0289 (6) | −0.0001 (5) | 0.0062 (4) | −0.0108 (5) |
| C4 | 0.0221 (5) | 0.0356 (7) | 0.0196 (5) | 0.0033 (5) | 0.0047 (4) | −0.0066 (5) |
| C5 | 0.0193 (5) | 0.0274 (6) | 0.0191 (5) | 0.0030 (4) | 0.0059 (4) | 0.0009 (4) |
| C6 | 0.0145 (5) | 0.0192 (5) | 0.0191 (5) | 0.0019 (4) | 0.0044 (4) | −0.0006 (4) |
| C7 | 0.0188 (5) | 0.0180 (5) | 0.0168 (4) | 0.0043 (4) | 0.0017 (4) | 0.0031 (4) |
| C8 | 0.0181 (5) | 0.0218 (5) | 0.0198 (5) | 0.0028 (4) | 0.0063 (4) | 0.0013 (4) |
| C9 | 0.0190 (5) | 0.0185 (5) | 0.0188 (5) | −0.0020 (4) | 0.0065 (4) | 0.0020 (4) |
| C10 | 0.0309 (6) | 0.0198 (5) | 0.0237 (5) | 0.0078 (5) | 0.0027 (4) | 0.0046 (4) |
| C11 | 0.0255 (6) | 0.0398 (8) | 0.0349 (7) | 0.0099 (6) | 0.0035 (5) | 0.0022 (6) |
| C12 | 0.0267 (6) | 0.0230 (6) | 0.0254 (5) | −0.0043 (5) | 0.0097 (4) | 0.0039 (4) |
| C13 | 0.0243 (6) | 0.0473 (8) | 0.0403 (7) | −0.0084 (6) | 0.0071 (5) | 0.0031 (6) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—C9 | 1.6591 (11) | C5—H5 | 0.9500 |
| S2—C7 | 1.6587 (11) | C7—C8 | 1.5150 (15) |
| N1—C9 | 1.3437 (15) | C8—C9 | 1.5131 (15) |
| N1—C1 | 1.4329 (13) | C8—H8A | 0.9900 |
| N1—C10 | 1.4803 (14) | C8—H8B | 0.9900 |
| N2—C7 | 1.3506 (14) | C10—C11 | 1.5118 (18) |
| N2—C6 | 1.4329 (14) | C10—H10A | 0.9900 |
| N2—C12 | 1.4805 (14) | C10—H10B | 0.9900 |
| C1—C2 | 1.3976 (15) | C11—H11A | 0.9800 |
| C1—C6 | 1.4008 (15) | C11—H11B | 0.9800 |
| C2—C3 | 1.3886 (17) | C11—H11C | 0.9800 |
| C2—H2 | 0.9500 | C12—C13 | 1.5157 (17) |
| C3—C4 | 1.3858 (19) | C12—H12A | 0.9900 |

| | | | |
|---|---|---|---|
| C3—H3 | 0.9500 | C12—H12B | 0.9900 |
| C4—C5 | 1.3815 (17) | C13—H13A | 0.9800 |
| C4—H4 | 0.9500 | C13—H13B | 0.9800 |
| C5—C6 | 1.4030 (15) | C13—H13C | 0.9800 |

| | | | |
|---|---|---|---|
| C9—N1—C1 | 121.84 (9) | C9—C8—H8B | 110.7 |
| C9—N1—C10 | 120.88 (9) | C7—C8—H8B | 110.7 |
| C1—N1—C10 | 117.06 (9) | H8A—C8—H8B | 108.8 |
| C7—N2—C6 | 122.11 (9) | N1—C9—C8 | 114.72 (9) |
| C7—N2—C12 | 120.02 (10) | N1—C9—S1 | 124.58 (8) |
| C6—N2—C12 | 117.86 (9) | C8—C9—S1 | 120.56 (8) |
| C2—C1—C6 | 119.65 (10) | N1—C10—C11 | 110.88 (10) |
| C2—C1—N1 | 118.31 (10) | N1—C10—H10A | 109.5 |
| C6—C1—N1 | 122.03 (9) | C11—C10—H10A | 109.5 |
| C3—C2—C1 | 120.45 (11) | N1—C10—H10B | 109.5 |
| C3—C2—H2 | 119.8 | C11—C10—H10B | 109.5 |
| C1—C2—H2 | 119.8 | H10A—C10—H10B | 108.1 |
| C4—C3—C2 | 119.84 (11) | C10—C11—H11A | 109.5 |
| C4—C3—H3 | 120.1 | C10—C11—H11B | 109.5 |
| C2—C3—H3 | 120.1 | H11A—C11—H11B | 109.5 |
| C5—C4—C3 | 120.34 (11) | C10—C11—H11C | 109.5 |
| C5—C4—H4 | 119.8 | H11A—C11—H11C | 109.5 |
| C3—C4—H4 | 119.8 | H11B—C11—H11C | 109.5 |
| C4—C5—C6 | 120.55 (11) | N2—C12—C13 | 111.43 (10) |
| C4—C5—H5 | 119.7 | N2—C12—H12A | 109.3 |
| C6—C5—H5 | 119.7 | C13—C12—H12A | 109.3 |
| C1—C6—C5 | 119.09 (10) | N2—C12—H12B | 109.3 |
| C1—C6—N2 | 122.18 (9) | C13—C12—H12B | 109.3 |
| C5—C6—N2 | 118.72 (10) | H12A—C12—H12B | 108.0 |
| N2—C7—C8 | 115.48 (9) | C12—C13—H13A | 109.5 |
| N2—C7—S2 | 124.50 (9) | C12—C13—H13B | 109.5 |
| C8—C7—S2 | 119.93 (8) | H13A—C13—H13B | 109.5 |
| C9—C8—C7 | 105.35 (9) | C12—C13—H13C | 109.5 |
| C9—C8—H8A | 110.7 | H13A—C13—H13C | 109.5 |
| C7—C8—H8A | 110.7 | H13B—C13—H13C | 109.5 |

| | | | |
|---|---|---|---|
| C9—N1—C1—C2 | 131.40 (11) | C12—N2—C6—C5 | 47.51 (13) |
| C10—N1—C1—C2 | −54.03 (14) | C6—N2—C7—C8 | −7.63 (14) |
| C9—N1—C1—C6 | −49.55 (15) | C12—N2—C7—C8 | 173.63 (9) |
| C10—N1—C1—C6 | 125.02 (11) | C6—N2—C7—S2 | 175.84 (8) |
| C6—C1—C2—C3 | −2.23 (17) | C12—N2—C7—S2 | −2.90 (14) |
| N1—C1—C2—C3 | 176.84 (10) | N2—C7—C8—C9 | −71.66 (11) |
| C1—C2—C3—C4 | −0.26 (18) | S2—C7—C8—C9 | 105.04 (9) |
| C2—C3—C4—C5 | 2.27 (18) | C1—N1—C9—C8 | −0.07 (15) |
| C3—C4—C5—C6 | −1.77 (17) | C10—N1—C9—C8 | −174.43 (10) |
| C2—C1—C6—C5 | 2.70 (16) | C1—N1—C9—S1 | 175.67 (8) |
| N1—C1—C6—C5 | −176.34 (10) | C10—N1—C9—S1 | 1.30 (15) |
| C2—C1—C6—N2 | −176.18 (10) | C7—C8—C9—N1 | 77.46 (11) |

| | | | |
|---|---|---|---|
| N1—C1—C6—N2 | 4.78 (16) | C7—C8—C9—S1 | −98.46 (10) |
| C4—C5—C6—C1 | −0.73 (16) | C9—N1—C10—C11 | 87.54 (13) |
| C4—C5—C6—N2 | 178.20 (10) | C1—N1—C10—C11 | −87.08 (12) |
| C7—N2—C6—C1 | 47.63 (15) | C7—N2—C12—C13 | −85.53 (13) |
| C12—N2—C6—C1 | −133.60 (11) | C6—N2—C12—C13 | 95.68 (12) |
| C7—N2—C6—C5 | −131.26 (11) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C3—H3···S1$^{i}$ | 0.95 | 2.86 | 3.6474 (13) | 141 |
| C12—H12*A*···S1$^{ii}$ | 0.99 | 2.87 | 3.4887 (13) | 121 |

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