

# Crystal structure and Hirshfeld surface analysis of 1-(2,4-dichlorobenzyl)-5-methyl-*N*-(thiophene-2-sulfonyl)-1*H*-pyrazole-3-carboxamide

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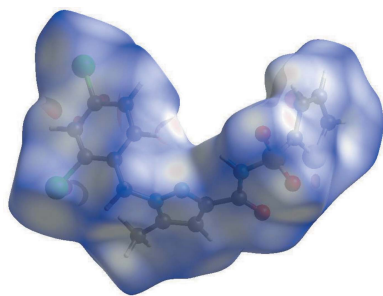
**CCDC reference:** 1839201

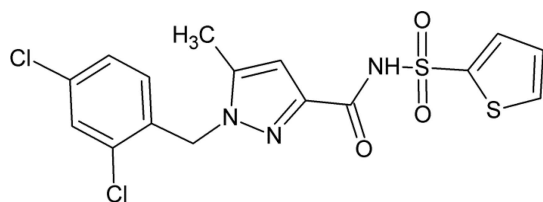
**Supporting information:** this article has supporting information at journals.iucr.org/e

In the title compound, C<sub>16</sub>H<sub>13</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub>, the thiophene ring is disordered in a 0.762 (3):0.238 (3) ratio by an approximate 180° rotation of the ring around the S—C bond linking the ring to the sulfonyl unit. The dichlorobenzene group is also disordered over two sets of sites with the same occupancy ratio. The molecular conformation is stabilized by intramolecular C—H···Cl and C—H···N hydrogen bonds, forming rings with graph-set notation *S*(5). In the crystal, pairs of molecules are linked by N—H···O and C—H···O hydrogen bonds, forming inversion dimers with graph-set notation *R*<sub>2</sub><sup>2</sup>(8) and *R*<sub>1</sub><sup>2</sup>(11), which are connected by C—H···O hydrogen-bonding interactions into ribbons parallel to (100). The ribbons are further connected into a three-dimensional network by C—H··· $\pi$  interactions and  $\pi$ – $\pi$  stacking interactions between benzene and thiophene rings, with centroid-to-centroid distances of 3.865 (2), 3.867 (7) and 3.853 (2) Å. Hirshfeld surface analysis has been used to confirm and quantify the supramolecular interactions.

## 1. Chemical context

The pyrazole *core* structure has been widely used as a common heterocyclic scaffold in medicinal chemistry to produce novel drug candidates with a great variety of pharmacological activities including anti-inflammatory, antiplatelet, anticancer, antimycobacterial, antidepressant and anticonvulsant properties (Küçükgül & Şenkardeş, 2015; Çalışkan *et al.*, 2013; Ding *et al.*, 2009; Baraldi *et al.*, 2004; Palaska *et al.*, 2008). Among them, pyrazole-carboxamide derivatives have been shown to exhibit antimycobacterial, antifungal and antiviral activities (Sun & Zhou, 2015; Yan *et al.*, 2018; Comber *et al.*, 1992). In the course of our ongoing research into bioactive pyrazole derivatives (Banoğlu *et al.*, 2005; Şüküroğlu *et al.*, 2005; Ergün *et al.*, 2010; Çalışkan *et al.*, 2011; Levent *et al.*, 2013; Cankara Pırol *et al.*, 2014), we have relied on the aforementioned biological properties of pyrazole-carboxamides and designed novel pyrazole-3-carboxamide derivatives for their potential antimicrobial activity. In this work, we report the crystallographic characterization and Hirshfeld surface analysis of one of these compounds bearing the 2,4-dichlorobenzyl substituent at one of the pyrazole nitrogen atoms.



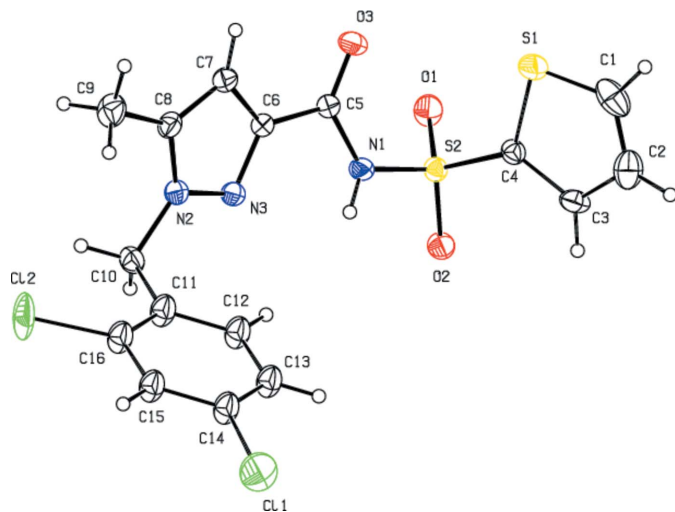


## 2. Structural commentary

In the molecule of the title compound (Fig. 1), the dihedral angles between the planes of the pyrazole ring *A* (N2/N3/C6–C8), the major and minor components *B* (S1/C1–C4) and *B'* (S1A/C1/C2/C3A/C4) of the disordered thiophene ring, and the disordered benzene ring *C* (C11–C16) and *C'* (C11A–C16A) are  $A/B = 67.62$  (16)°,  $A/B' = 68.1$  (5)°,  $B/B' = 3.3$  (5)°,  $A/C = 70.09$  (16)°,  $B/C = 83.06$  (19)° and  $B'/C = 80.2$  (5)°,  $A/C' = 78.4$  (4)°,  $B/C' = 77.3$  (4)° and  $B'/C' = 74.2$  (6)°. The molecular conformation is stabilized by intramolecular C–H···Cl and C–H···N hydrogen bonds (Table 1), forming rings with graph-set notation  $S(5)$ .

## 3. Supramolecular features

In the crystal, pairs of molecules are linked by intermolecular N–H···O and C–H···O hydrogen bonds (Table 1; Figs. 2 and 3), forming inversion dimers with graph-set notation  $R_2^2(8)$  and  $R_2^2(11)$ , which are connected by C–H···O hydrogen-bonding interactions into ribbons parallel to (100). The ribbons are further connected into a three-dimensional network by C–H··· $\pi$  interactions (Table 1) and  $\pi$ – $\pi$  stacking interactions between the benzene and thiophene rings, with centroid-to-centroid distances of 3.865 (2) Å for  $Cg1 \cdots Cg1^v$ , 3.867 (7) Å for  $Cg2 \cdots Cg2^v$  and 3.853 (2) Å for  $Cg4 \cdots Cg4^{vi}$  where  $Cg1$ ,  $Cg2$  and  $Cg4$  are the centroids of the thiophene



**Figure 1**  
The molecular structure of the title compound with displacement ellipsoids for non-H atoms drawn at the 30% probability level. The minor components of the disordered thiophene and dichlorobenzene groups have been omitted.

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

$Cg1$  is the centroid of the major component (S1/C1–C4) of the disordered thiophene ring.

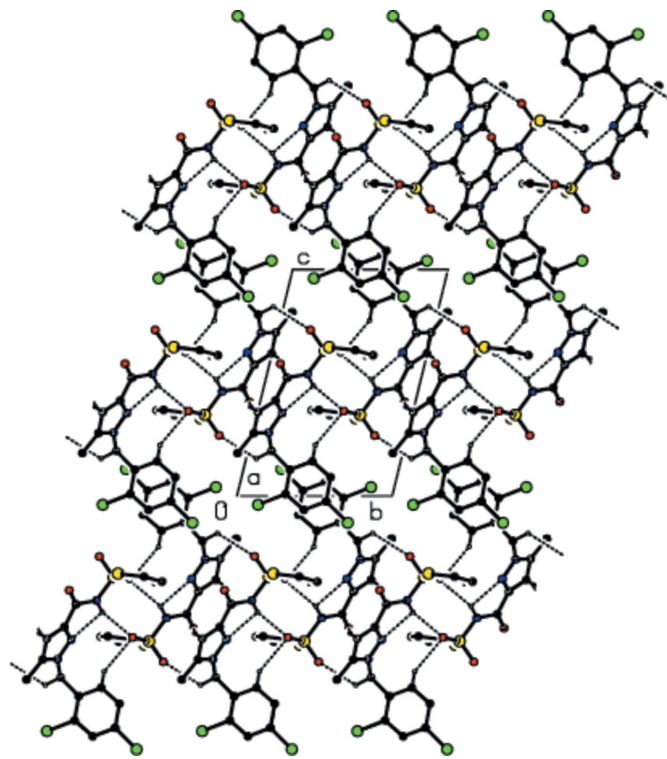
$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1–H1N···O2 <sup>i</sup>	0.84 (3)	2.27 (3)	3.029 (3)	150 (3)
C7–H7···O3 <sup>iii</sup>	0.93	2.59	3.437 (3)	152
C10–H10B···O1 <sup>iii</sup>	0.97	2.52	3.141 (3)	122
C12–H12···N3	0.93	2.61	3.224 (3)	124
C12–H12···O2 <sup>i</sup>	0.93	2.51	3.348 (3)	150
C15–H15···Cg1 <sup>iv</sup>	0.93	2.97	3.893 (3)	174
C15A–H15A···Cg1 <sup>iv</sup>	0.93	2.95	3.836 (8)	159

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

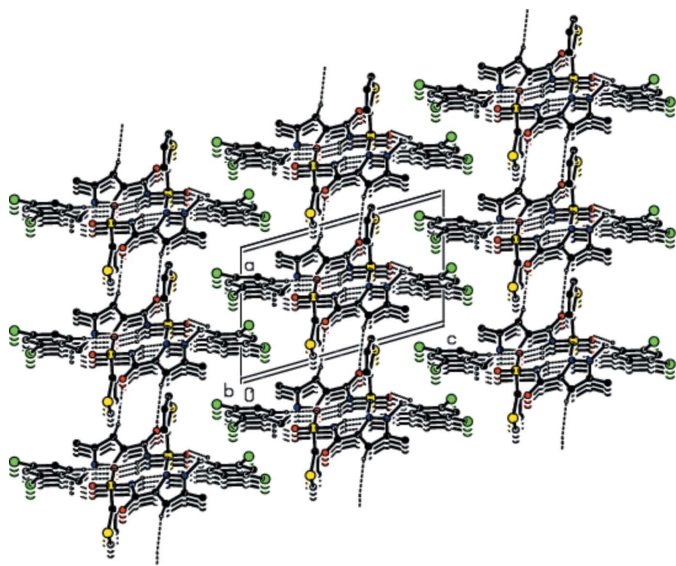
ring *B*, the thiophene ring *B'* and the benzene ring *C* [symmetry codes: (v)  $2 - x, 1 - y, 1 - z$ ; (vi)  $1 - x, 1 - y, -z$ ].

## 4. Hirshfeld surface analysis

A Hirshfeld surface analysis (Hirshfeld, 1977; Spackman & Jayatilaka, 2009) of the title compound was carried out to investigate the location of atoms with potential to form hydrogen bonds and the quantitative ratio of these interactions. *CrystalExplorer17.5* (Turner *et al.*, 2017) was used to generate the Hirshfeld surface and two-dimensional fingerprint plots (Parkin *et al.*, 2007; Rohl *et al.*, 2008), using the



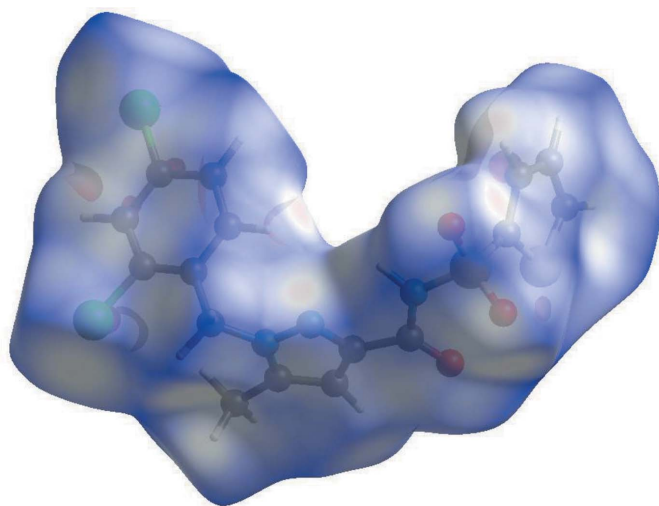
**Figure 2**  
Crystal structure of the title compound viewed along the *a* axis. Dashed lines show hydrogen-bonding interactions. The minor components of the disordered groups have been omitted.



**Figure 3**  
Crystal structure of the title compound viewed along the *b* axis. Dashed lines show hydrogen-bonding interactions. The minor components of the disordered groups have been omitted.

atomic coordinates of the major disorder component of the disordered atoms (Figs. 4 and 5). The electrostatic potentials were calculated using *TONTO* (Spackman *et al.*, 2009) integrated into *CrystalExplorer*, wherein the respective experimental structure was used as the input to *TONTO*. Further, the electrostatic potentials were mapped on Hirshfeld surfaces using the STO-3G basis set at the Hartree–Fock level of theory.

The intermolecular distance information on the surface can be condensed into a two-dimensional histogram of  $d_e$  and  $d_i$ , which is a unique identifier for molecules in a crystal structure, and is known as a fingerprint plot. Instead of plotting  $d_e$  and  $d_i$  on the Hirshfeld surface, contact distances are normalized in

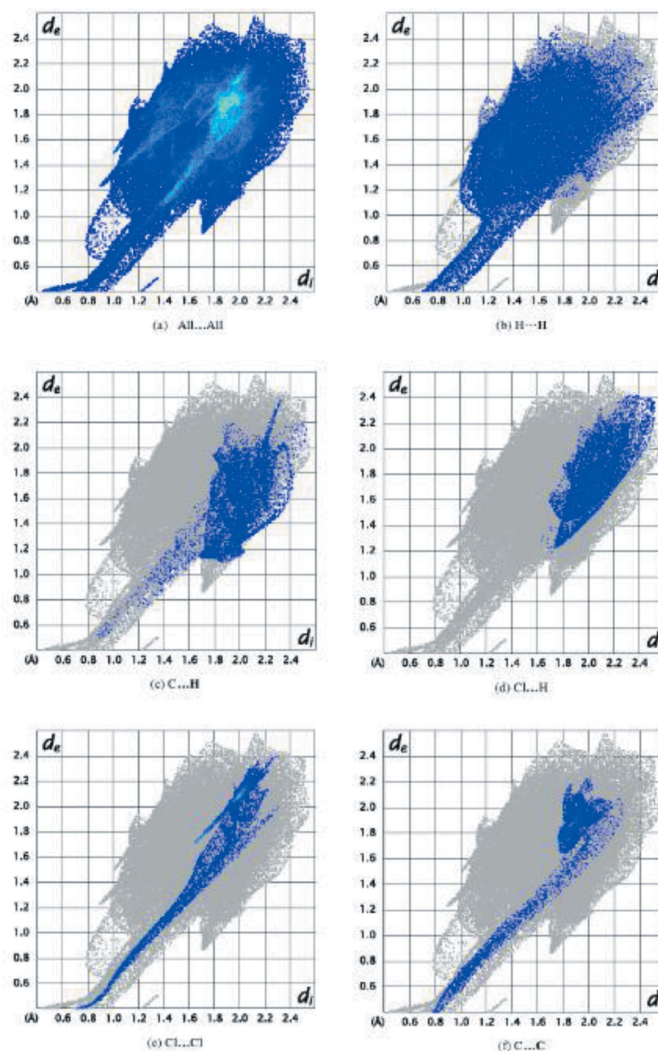


**Figure 4**  
The Hirshfeld surface of the title compound mapped over  $d_{\text{norm}}$ .

*CrystalExplorer* using the van der Waals radius of the appropriate internal ( $r_i^{\text{vdw}}$ ) and external ( $r_e^{\text{vdw}}$ ) atom of the surface:

$$d_{\text{norm}} = (d_i - r_i^{\text{vdw}})/r_i^{\text{vdw}} + (d_e - r_e^{\text{vdw}})/r_e^{\text{vdw}}$$

The molecular Hirshfeld surfaces were obtained using a standard (high) surface resolution with the three-dimensional  $d_{\text{norm}}$  surfaces mapped over a fixed colour scale of  $-1.9033$  (red) to  $1.1934$  (blue). In the fingerprint plots (Rohl *et al.*, 2008), shown in Fig. 5, the points indicated by *b*, *c*, *d* and *e* correspond to  $\text{H}\cdots\text{H}$ ,  $\text{C}\cdots\text{H}$ ,  $\text{Cl}\cdots\text{H}$ ,  $\text{Cl}\cdots\text{Cl}$  and  $\text{C}\cdots\text{C}$  interactions with relative contributions of 28.4, 7.0, 6.8, 6.5 and 5.7%, respectively. These types of interactions add up to 54.4% of the intermolecular contacts of the Hirshfeld surface area. The remaining contributions (8.3%) correspond to  $\text{C}\cdots\text{Cl}$  (1.3%),  $\text{N}\cdots\text{C}$  (1.3%) and other less important interactions (<1%).  $\text{C}\cdots\text{C}$  contacts correspond to intermolecular  $\pi$ – $\pi$  interactions. The occurrence of non-high interaction rates can be attributed to the fact that the small disordered portion of the molecule is not considered.



**Figure 5**  
The two-dimensional fingerprint plots of the title compound, showing (a) all interactions, and delineated into (b)  $\text{H}\cdots\text{H}$ , (c)  $\text{C}\cdots\text{H}$ , (d)  $\text{Cl}\cdots\text{H}$ , (e)  $\text{Cl}\cdots\text{Cl}$  and (f)  $\text{C}\cdots\text{C}$  interactions. The outline of the full fingerprint plots is shown in grey.  $d_i$  is the closest internal distance from a given point on the Hirshfeld surface and  $d_e$  is the closest external contact.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>16</sub> H <sub>13</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>3</sub> S <sub>2</sub>
<i>M</i> <sub>r</sub>	430.31
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.2706 (4), 8.7726 (4), 13.6433 (7)
$\alpha$ , $\beta$ , $\gamma$ (°)	76.091 (2), 74.610 (2), 87.970 (2)
<i>V</i> (Å <sup>3</sup> )	925.98 (8)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.60
Crystal size (mm)	0.99 × 0.68 × 0.52
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2007)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.60, 0.75
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	19595, 4598, 4134
<i>R</i> <sub>int</sub>	0.024
(sin $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.668
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.056, 0.155, 1.03
No. of reflections	4598
No. of parameters	216
No. of restraints	14
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	1.20, -0.82

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

## 5. Database survey

All bond lengths and angles are within normal ranges and are similar to those reported for related molecules such as *trans-rac*-[1-oxo-2-phenethyl-3-(2-thienyl)-1,2,3,4-tetrahydroisoquinolin-4-yl]methyl 4-methylbenzenesulfonate (Akkurt *et al.*, 2008), 2-benzenesulfonamidobenzoic acid (Asiri *et al.*, 2009), propyl 2-(4-methylbenzenesulfonamido)benzoate (Mustafa, Khan *et al.*, 2012), 2-[4-[acetyl(ethyl)amino]benzenesulfonamido]benzoic acid (Mustafa, Muhmood *et al.*, 2012), 2-(5-bromopyridin-3-yl)-5-[3-(4,5,6,7-tetrahydrothieno[3,2-*c*]pyridine-5-ylsulfonyl)thiophen-2-yl]-1,3,4-oxadiazole (Fun *et al.*, 2011a) and 2-(biphenyl-4-yl)-5-[3-(4,5,6,7-tetrahydrothieno[3,2-*c*]pyridine-5-ylsulfonyl) thiophen-2-yl]-1,3,4-oxadiazole (Fun *et al.*, 2011b).

## 6. Synthesis and crystallization

To a solution of methyl 1-(2,4-dichlorobenzyl)-5-methyl-1*H*-pyrazole-3-carboxylate (200 mg, 0.70 mmol, 1 equiv.) in dichloromethane (DCM) were added 2-thiophenesulfonamide (126 mg, 0.77 mmol, 1.1 equiv.), 1-ethyl-3-(3-dimethylamino-propyl)carbodiimide (EDC; 148 mg, 0.77 mmol, 1.1 equiv.) and 4-dimethyl-aminopyridine (DMAP; 17.8 mg, 0.14 mmol, 0.2 equiv.), and the resulting mixture was stirred overnight at room temperature. Upon completion of the reaction, the reaction mixture was partitioned between DCM and water.

The collected organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to give the crude compound, which was purified with automated-flash chromatography (120.6 mg, 39.95%). The obtained product was recrystallized from hexane and ethyl acetate (4:1), m.p. 464.8–465.3 K. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.24 (3H, *s*), 5.33 (2H, *s*), 6.64 (2H, *m*), 7.12 (1H, *m*), 7.21 (1H, *dd*, *J* = 8.4, 2.1 Hz), 7.45 (1H, *d*, *J* = 2.1 Hz), 7.69 (1H, *dd*, *J* = 5.1, 1.2 Hz), 7.97 (1H, *dd*, *J* = 3.9, 1.2 Hz), 9.29 (1H, *bs*); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 11.2, 50.5, 107.6, 127.3, 127.9, 129.1, 129.6, 131.7, 132.9, 133.8, 134.8, 135.1, 139.2, 142.0, 143.5, 158.4. HRMS *m/z* calculated for C<sub>16</sub>H<sub>13</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub> [*M* + *H*]<sup>+</sup> 429.9854; found: 429.9857.

## 7. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms bound to carbon atoms were positioned geometrically and treated as riding with C–H = 0.93–0.97 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) or 1.5*U*<sub>eq</sub>(C) for methyl H atoms. A rotating model was used for the methyl group. The nitrogen-bound H atom (H1N) was located in a difference-Fourier map and refined with the constraint N1–H1N = 0.84 (3) Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(N). The thiophene ring is rotationally disordered by approximately 180° over two positions, the ratio of refined occupancies being 0.762 (3):0.238 (3). The dichlorobenzene group of the title compound is also disordered over two sets of sites with the same occupancy ratio. The disordered dichlorobenzene groups (C: C11–C16 and C': C11A–C16A) were refined as rigid hexagons with bond lengths of 1.39 Å. The displacement ellipsoids for the corresponding carbon atoms in the disordered dichlorobenzene groups were constrained by using the EADP command. Six outliers (633, 530, 130, 515, 561, 520) were omitted in the final cycles of refinement.

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## supporting information

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## Crystal structure and Hirshfeld surface analysis of 1-(2,4-dichlorobenzyl)-5-methyl-*N*-(thiophene-2-sulfonyl)-1*H*-pyrazole-3-carboxamide

Abdullah Aydin, Mehmet Akkurt, Zehra Tugce Gur and Erden Banoğlu

### Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE* (Bruker, 2007); program(s) used to solve structure: *SHELXT-2014* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015*b*); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2009) and *WinGX* (Farrugia, 2012).

### 1-(2,4-Dichlorobenzyl)-5-methyl-*N*-(thiophene-2-sulfonyl)-1*H*-pyrazole-3-carboxamide

#### Crystal data

$C_{16}H_{13}Cl_2N_3O_3S_2$   
 $M_r = 430.31$   
 Triclinic,  $P\bar{1}$   
 Hall symbol:  $-P\ 1$   
 $a = 8.2706$  (4) Å  
 $b = 8.7726$  (4) Å  
 $c = 13.6433$  (7) Å  
 $\alpha = 76.091$  (2)°  
 $\beta = 74.610$  (2)°  
 $\gamma = 87.970$  (2)°  
 $V = 925.98$  (8) Å<sup>3</sup>

$Z = 2$   
 $F(000) = 440$   
 $D_x = 1.543$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 9888 reflections  
 $\theta = 2.4$ – $28.3$ °  
 $\mu = 0.60$  mm<sup>-1</sup>  
 $T = 296$  K  
 Prism, translucent light white  
 $0.99 \times 0.68 \times 0.52$  mm

#### Data collection

Bruker APEXII CCD  
 diffractometer  
 Radiation source: sealed tube  
 Graphite monochromator  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2007)  
 $T_{\min} = 0.60$ ,  $T_{\max} = 0.75$

19595 measured reflections  
 4598 independent reflections  
 4134 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.024$   
 $\theta_{\max} = 28.4$ °,  $\theta_{\min} = 1.6$ °  
 $h = -10 \rightarrow 11$   
 $k = -11 \rightarrow 11$   
 $l = -17 \rightarrow 18$

#### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.056$   
 $wR(F^2) = 0.155$   
 $S = 1.03$   
 4598 reflections  
 216 parameters  
 14 restraints

Hydrogen site location: mixed  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.082P)^2 + 0.8819P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 1.20$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.82$  e Å<sup>-3</sup>

*Special details*

**Geometry.** Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

**Refinement.** Refinement on  $F^2$  for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses 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 observed criterion of  $F^2 > 2\sigma(F^2)$  is used only for calculating -R-factor-obs 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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	1.0018 (3)	0.5302 (5)	0.6433 (2)	0.0643 (8)	
H1	1.109594	0.540142	0.650187	0.077*	
C2	0.9085 (4)	0.6538 (4)	0.6217 (3)	0.0615 (8)	
H2	0.943899	0.757761	0.609474	0.074*	
C3	0.7555 (6)	0.6082 (6)	0.6199 (4)	0.0426 (11)	0.762 (3)
H3	0.670625	0.678061	0.610153	0.051*	0.762 (3)
S1	0.91332 (19)	0.35743 (15)	0.65722 (17)	0.0492 (3)	0.762 (3)
C3A	0.901 (2)	0.382 (2)	0.655 (2)	0.0426 (11)	0.238 (3)
H3A	0.933907	0.278893	0.670858	0.051*	0.238 (3)
S1A	0.7356 (7)	0.6272 (6)	0.6034 (4)	0.0492 (3)	0.238 (3)
C4	0.7359 (3)	0.4413 (3)	0.63434 (16)	0.0334 (4)	
C5	0.7050 (3)	0.1354 (2)	0.52207 (17)	0.0330 (4)	
C6	0.7152 (3)	0.0968 (2)	0.42142 (16)	0.0313 (4)	
C7	0.8307 (3)	0.0022 (3)	0.37032 (19)	0.0375 (5)	
H7	0.916655	-0.053427	0.393564	0.045*	
C8	0.7892 (3)	0.0094 (3)	0.27811 (18)	0.0361 (4)	
C9	0.8648 (4)	-0.0637 (4)	0.1890 (2)	0.0529 (6)	
H9A	0.794588	-0.150751	0.192409	0.079*	
H9B	0.974150	-0.100242	0.193074	0.079*	
H9C	0.874250	0.012686	0.124042	0.079*	
C10	0.5646 (3)	0.1512 (3)	0.19870 (18)	0.0397 (5)	
H10A	0.448790	0.169220	0.231841	0.048*	
H10B	0.565068	0.066145	0.164493	0.048*	
C11	0.6400 (5)	0.2998 (3)	0.1159 (2)	0.0466 (3)	0.762 (3)
C12	0.6577 (4)	0.4311 (3)	0.15290 (16)	0.0466 (3)	0.762 (3)
H12	0.629582	0.423813	0.224578	0.056*	0.762 (3)
C13	0.7173 (4)	0.5732 (3)	0.08277 (18)	0.0466 (3)	0.762 (3)
H13	0.729125	0.660962	0.107532	0.056*	0.762 (3)
C14	0.7593 (4)	0.5840 (2)	-0.02436 (17)	0.0466 (3)	0.762 (3)
C15	0.7416 (5)	0.4528 (3)	-0.06137 (17)	0.0466 (3)	0.762 (3)
H15	0.769664	0.460061	-0.133046	0.056*	0.762 (3)
C16	0.6819 (6)	0.3107 (3)	0.0088 (3)	0.0466 (3)	0.762 (3)
Cl1	0.8269 (3)	0.7564 (2)	-0.11887 (17)	0.0835 (5)	0.762 (3)
Cl2	0.6424 (5)	0.1501 (4)	-0.0388 (2)	0.0805 (7)	0.762 (3)
C11A	0.6465 (15)	0.3022 (11)	0.1193 (7)	0.0466 (3)	0.238 (3)

C12A	0.7063 (12)	0.4320 (11)	0.1423 (5)	0.0466 (3)	0.238 (3)
H12A	0.696770	0.433593	0.211501	0.056*	0.238 (3)
C13A	0.7802 (12)	0.5595 (9)	0.0618 (6)	0.0466 (3)	0.238 (3)
H13A	0.820202	0.646324	0.077136	0.056*	0.238 (3)
C14A	0.7945 (12)	0.5571 (9)	-0.0417 (5)	0.0466 (3)	0.238 (3)
C15A	0.7347 (15)	0.4273 (11)	-0.0646 (6)	0.0466 (3)	0.238 (3)
H15A	0.744229	0.425767	-0.133838	0.056*	0.238 (3)
C16A	0.6608 (17)	0.2999 (11)	0.0159 (9)	0.0466 (3)	0.238 (3)
Cl1A	0.8896 (10)	0.7355 (9)	-0.1136 (7)	0.0835 (5)	0.238 (3)
Cl2A	0.6826 (18)	0.1514 (15)	-0.0300 (9)	0.0805 (7)	0.238 (3)
N1	0.6005 (2)	0.2605 (2)	0.53833 (15)	0.0363 (4)	
H1N	0.571 (4)	0.317 (3)	0.4869 (18)	0.044*	
N2	0.6550 (2)	0.1036 (2)	0.27928 (14)	0.0340 (4)	
N3	0.6080 (2)	0.1593 (2)	0.36579 (14)	0.0334 (4)	
O1	0.5273 (2)	0.2101 (2)	0.73271 (13)	0.0479 (4)	
O2	0.4310 (2)	0.4460 (2)	0.62514 (13)	0.0412 (4)	
O3	0.7814 (2)	0.0698 (2)	0.58384 (14)	0.0473 (4)	
S2	0.55880 (6)	0.33499 (6)	0.64141 (4)	0.03159 (15)	

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.1094 (16)	0.0562 (7)	0.0754 (7)	-0.0290 (10)	-0.0317 (10)	0.0150 (5)
Cl1A	0.1094 (16)	0.0562 (7)	0.0754 (7)	-0.0290 (10)	-0.0317 (10)	0.0150 (5)
Cl2	0.144 (2)	0.0649 (5)	0.0438 (7)	-0.0339 (10)	-0.0276 (8)	-0.0255 (5)
Cl2A	0.144 (2)	0.0649 (5)	0.0438 (7)	-0.0339 (10)	-0.0276 (8)	-0.0255 (5)
S1	0.0461 (5)	0.0507 (7)	0.0605 (6)	0.0166 (4)	-0.0260 (4)	-0.0205 (6)
S1A	0.0461 (5)	0.0507 (7)	0.0605 (6)	0.0166 (4)	-0.0260 (4)	-0.0205 (6)
S2	0.0325 (3)	0.0336 (3)	0.0302 (3)	0.0020 (2)	-0.0086 (2)	-0.0102 (2)
O1	0.0609 (11)	0.0441 (9)	0.0348 (8)	-0.0091 (8)	-0.0098 (7)	-0.0038 (7)
O2	0.0342 (8)	0.0474 (9)	0.0468 (9)	0.0105 (7)	-0.0122 (7)	-0.0204 (7)
O3	0.0556 (10)	0.0487 (10)	0.0485 (10)	0.0187 (8)	-0.0304 (8)	-0.0160 (8)
N1	0.0458 (10)	0.0360 (9)	0.0336 (9)	0.0126 (8)	-0.0186 (8)	-0.0135 (7)
N2	0.0386 (9)	0.0332 (8)	0.0323 (9)	0.0031 (7)	-0.0116 (7)	-0.0099 (7)
N3	0.0366 (9)	0.0338 (8)	0.0330 (9)	0.0061 (7)	-0.0125 (7)	-0.0108 (7)
C1	0.0361 (12)	0.105 (3)	0.0567 (17)	-0.0026 (14)	-0.0139 (11)	-0.0267 (17)
C2	0.0577 (16)	0.0581 (17)	0.0667 (19)	-0.0200 (14)	-0.0091 (14)	-0.0164 (14)
C3	0.0345 (19)	0.0394 (19)	0.051 (2)	-0.0035 (14)	-0.0204 (15)	0.0060 (15)
C3A	0.0345 (19)	0.0394 (19)	0.051 (2)	-0.0035 (14)	-0.0204 (15)	0.0060 (15)
C4	0.0306 (9)	0.0381 (10)	0.0336 (10)	0.0034 (8)	-0.0096 (7)	-0.0122 (8)
C5	0.0344 (10)	0.0310 (9)	0.0369 (10)	0.0036 (7)	-0.0137 (8)	-0.0103 (8)
C6	0.0332 (9)	0.0285 (9)	0.0344 (10)	0.0027 (7)	-0.0119 (8)	-0.0088 (8)
C7	0.0361 (10)	0.0351 (10)	0.0468 (12)	0.0078 (8)	-0.0157 (9)	-0.0158 (9)
C8	0.0372 (10)	0.0317 (10)	0.0411 (11)	0.0031 (8)	-0.0091 (8)	-0.0139 (8)
C9	0.0538 (14)	0.0576 (15)	0.0525 (15)	0.0090 (12)	-0.0087 (12)	-0.0298 (13)
C10	0.0471 (12)	0.0413 (11)	0.0348 (11)	-0.0009 (9)	-0.0173 (9)	-0.0094 (9)
C11	0.0639 (8)	0.0396 (6)	0.0367 (6)	-0.0054 (6)	-0.0098 (5)	-0.0130 (5)
C11A	0.0639 (8)	0.0396 (6)	0.0367 (6)	-0.0054 (6)	-0.0098 (5)	-0.0130 (5)



C12	0.0639 (8)	0.0396 (6)	0.0367 (6)	-0.0054 (6)	-0.0098 (5)	-0.0130 (5)
C12A	0.0639 (8)	0.0396 (6)	0.0367 (6)	-0.0054 (6)	-0.0098 (5)	-0.0130 (5)
C13	0.0639 (8)	0.0396 (6)	0.0367 (6)	-0.0054 (6)	-0.0098 (5)	-0.0130 (5)
C13A	0.0639 (8)	0.0396 (6)	0.0367 (6)	-0.0054 (6)	-0.0098 (5)	-0.0130 (5)
C14	0.0639 (8)	0.0396 (6)	0.0367 (6)	-0.0054 (6)	-0.0098 (5)	-0.0130 (5)
C14A	0.0639 (8)	0.0396 (6)	0.0367 (6)	-0.0054 (6)	-0.0098 (5)	-0.0130 (5)
C15	0.0639 (8)	0.0396 (6)	0.0367 (6)	-0.0054 (6)	-0.0098 (5)	-0.0130 (5)
C15A	0.0639 (8)	0.0396 (6)	0.0367 (6)	-0.0054 (6)	-0.0098 (5)	-0.0130 (5)
C16	0.0639 (8)	0.0396 (6)	0.0367 (6)	-0.0054 (6)	-0.0098 (5)	-0.0130 (5)
C16A	0.0639 (8)	0.0396 (6)	0.0367 (6)	-0.0054 (6)	-0.0098 (5)	-0.0130 (5)

*Geometric parameters (Å, °)*

C11—C14	1.733 (3)	C10—C11	1.530 (4)
C11A—C14A	1.723 (12)	C11—C12	1.391 (4)
C12—C16	1.760 (5)	C11—C16	1.390 (5)
C12A—C16A	1.561 (17)	C11A—C16A	1.389 (15)
S1—C4	1.688 (3)	C11A—C12A	1.391 (14)
S1—C1	1.654 (4)	C12—C13	1.390 (4)
S1A—C4	1.583 (6)	C12A—C13A	1.390 (11)
S1A—C2	1.550 (7)	C13—C14	1.390 (3)
S2—O2	1.4362 (18)	C13A—C14A	1.391 (10)
S2—N1	1.641 (2)	C14—C15	1.390 (3)
S2—C4	1.733 (3)	C14A—C15A	1.390 (13)
S2—O1	1.4184 (18)	C15—C16	1.390 (4)
O3—C5	1.210 (3)	C15A—C16A	1.390 (14)
N1—C5	1.396 (3)	C1—H1	0.9300
N2—N3	1.343 (3)	C2—H2	0.9300
N2—C8	1.359 (3)	C3—H3	0.9300
N2—C10	1.461 (3)	C3A—H3A	0.9300
N3—C6	1.336 (3)	C7—H7	0.9300
C1—C2	1.329 (5)	C9—H9A	0.9600
C1—C3A	1.522 (19)	C9—H9C	0.9600
N1—H1N	0.84 (3)	C9—H9B	0.9600
C2—C3	1.349 (6)	C10—H10A	0.9700
C3—C4	1.439 (6)	C10—H10B	0.9700
C3A—C4	1.516 (19)	C12—H12	0.9300
C5—C6	1.472 (3)	C12A—H12A	0.9300
C6—C7	1.399 (3)	C13—H13	0.9300
C7—C8	1.376 (3)	C13A—H13A	0.9300
C8—C9	1.491 (4)	C15—H15	0.9300
C10—C11A	1.540 (10)	C15A—H15A	0.9300
C1—S1—C4	91.91 (16)	C11—C14—C15	115.95 (18)
C2—S1A—C4	96.3 (4)	C13—C14—C15	120.0 (2)
O1—S2—N1	108.73 (10)	C11A—C14A—C13A	104.5 (7)
O1—S2—C4	108.83 (11)	C11A—C14A—C15A	135.5 (6)
O1—S2—O2	120.05 (10)	C13A—C14A—C15A	120.0 (7)

O2—S2—C4	107.17 (12)	C14—C15—C16	120.0 (2)
N1—S2—C4	107.33 (10)	C14A—C15A—C16A	120.0 (8)
O2—S2—N1	104.06 (10)	C12—C16—C11	120.2 (3)
S2—N1—C5	126.32 (16)	C12—C16—C15	119.6 (3)
N3—N2—C8	112.91 (18)	C11—C16—C15	120.0 (3)
N3—N2—C10	119.06 (18)	C11A—C16A—C15A	120.0 (10)
C8—N2—C10	128.01 (19)	C12A—C16A—C11A	126.3 (10)
N2—N3—C6	104.17 (16)	C12A—C16A—C15A	107.6 (9)
S1—C1—C2	115.5 (2)	S1—C1—H1	122.00
C2—C1—C3A	108.6 (7)	C2—C1—H1	122.00
S2—N1—H1N	113.9 (18)	C3A—C1—H1	129.00
C5—N1—H1N	118.5 (18)	S1A—C2—H2	116.00
C1—C2—C3	110.9 (4)	C1—C2—H2	125.00
S1A—C2—C1	118.7 (4)	C3—C2—H2	125.00
C2—C3—C4	113.7 (4)	C2—C3—H3	123.00
C1—C3A—C4	104.5 (12)	C4—C3—H3	123.00
S1—C4—C3	107.9 (3)	C4—C3A—H3A	128.00
S2—C4—C3A	129.1 (7)	C1—C3A—H3A	128.00
S1A—C4—S2	119.4 (3)	C8—C7—H7	128.00
S2—C4—C3	128.3 (3)	C6—C7—H7	128.00
S1—C4—S2	123.50 (17)	C8—C9—H9A	109.00
S1A—C4—C3A	111.6 (8)	H9A—C9—H9B	109.00
O3—C5—C6	124.5 (2)	C8—C9—H9B	110.00
O3—C5—N1	122.7 (2)	C8—C9—H9C	110.00
N1—C5—C6	112.78 (19)	H9B—C9—H9C	109.00
C5—C6—C7	128.2 (2)	H9A—C9—H9C	109.00
N3—C6—C7	111.90 (19)	N2—C10—H10B	109.00
N3—C6—C5	119.91 (19)	C11—C10—H10A	109.00
C6—C7—C8	104.9 (2)	C11A—C10—H10A	110.00
C7—C8—C9	131.6 (3)	C11A—C10—H10B	111.00
N2—C8—C9	122.3 (2)	C11—C10—H10B	109.00
N2—C8—C7	106.1 (2)	N2—C10—H10A	109.00
N2—C10—C11A	110.0 (5)	H10A—C10—H10B	108.00
N2—C10—C11	113.2 (2)	C13—C12—H12	120.00
C10—C11—C12	116.2 (2)	C11—C12—H12	120.00
C10—C11—C16	123.7 (3)	C13A—C12A—H12A	120.00
C12—C11—C16	120.0 (2)	C11A—C12A—H12A	120.00
C10—C11A—C12A	126.4 (7)	C14—C13—H13	120.00
C10—C11A—C16A	113.6 (8)	C12—C13—H13	120.00
C12A—C11A—C16A	120.0 (9)	C14A—C13A—H13A	120.00
C11—C12—C13	120.0 (2)	C12A—C13A—H13A	120.00
C11A—C12A—C13A	120.0 (7)	C16—C15—H15	120.00
C12—C13—C14	120.0 (2)	C14—C15—H15	120.00
C12A—C13A—C14A	120.0 (8)	C14A—C15A—H15A	120.00
C11—C14—C13	123.98 (18)	C16A—C15A—H15A	120.00
C1—S1—C4—S2	-176.25 (16)	C2—C3—C4—S1	3.8 (5)
C1—S1—C4—C3	-2.0 (3)	C2—C3—C4—S2	177.7 (3)

C4—S1—C1—C2	-0.1 (3)	O3—C5—C6—C7	-12.2 (4)
O1—S2—N1—C5	-44.1 (2)	N1—C5—C6—N3	-11.7 (3)
O2—S2—N1—C5	-173.15 (18)	N1—C5—C6—C7	166.0 (2)
C4—S2—N1—C5	73.5 (2)	O3—C5—C6—N3	170.1 (2)
O2—S2—C4—S1	175.63 (16)	N3—C6—C7—C8	0.1 (3)
N1—S2—C4—S1	-73.11 (18)	C5—C6—C7—C8	-177.8 (2)
O1—S2—C4—C3	-128.6 (3)	C6—C7—C8—C9	179.3 (3)
O2—S2—C4—C3	2.6 (3)	C6—C7—C8—N2	-0.5 (3)
N1—S2—C4—C3	113.9 (3)	N2—C10—C11—C12	-55.0 (4)
O1—S2—C4—S1	44.39 (19)	N2—C10—C11—C16	128.4 (4)
S2—N1—C5—C6	179.75 (16)	C10—C11—C12—C13	-176.8 (3)
S2—N1—C5—O3	-2.0 (3)	C16—C11—C12—C13	0.0 (6)
C8—N2—C10—C11	-88.0 (3)	C10—C11—C16—C12	2.2 (6)
C8—N2—N3—C6	-0.6 (2)	C10—C11—C16—C15	176.6 (4)
N3—N2—C8—C7	0.7 (3)	C12—C11—C16—C12	-174.4 (3)
N3—N2—C10—C11	90.2 (2)	C12—C11—C16—C15	0.0 (7)
C10—N2—C8—C7	178.9 (2)	C11—C12—C13—C14	0.0 (5)
C10—N2—N3—C6	-179.01 (19)	C12—C13—C14—C11	177.4 (3)
C10—N2—C8—C9	-0.8 (4)	C12—C13—C14—C15	0.0 (5)
N3—N2—C8—C9	-179.1 (2)	C11—C14—C15—C16	-177.6 (3)
N2—N3—C6—C5	178.40 (18)	C13—C14—C15—C16	0.0 (6)
N2—N3—C6—C7	0.3 (2)	C14—C15—C16—C12	174.4 (3)
S1—C1—C2—C3	2.4 (4)	C14—C15—C16—C11	0.0 (7)
C1—C2—C3—C4	-4.0 (5)		

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

Cg1 is the centroid of the major component (S1/C1—C4) of the disordered thiophene ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N $\cdots$ N3	0.84 (3)	2.35 (3)	2.694 (3)	105 (2)
N1—H1N $\cdots$ O2 <sup>i</sup>	0.84 (3)	2.27 (3)	3.029 (3)	150 (3)
C7—H7 $\cdots$ O3 <sup>ii</sup>	0.93	2.59	3.437 (3)	152
C10—H10B $\cdots$ C12	0.97	2.60	3.134 (4)	115
C10—H10B $\cdots$ C12A	0.97	2.50	3.012 (12)	112
C10—H10B $\cdots$ O1 <sup>iii</sup>	0.97	2.52	3.141 (3)	122
C12—H12 $\cdots$ N3	0.93	2.61	3.224 (3)	124
C12—H12 $\cdots$ O2 <sup>i</sup>	0.93	2.51	3.348 (3)	150
C15—H15 $\cdots$ Cg1 <sup>iv</sup>	0.93	2.97	3.893 (3)	174
C15A—H15A $\cdots$ Cg1 <sup>iv</sup>	0.93	2.95	3.836 (8)	159

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