



Crystal structure and Hirshfeld surface analysis of *trans*-2,5-dimethylpiperazine-1,4-dium tetrachloridocobaltate(II)

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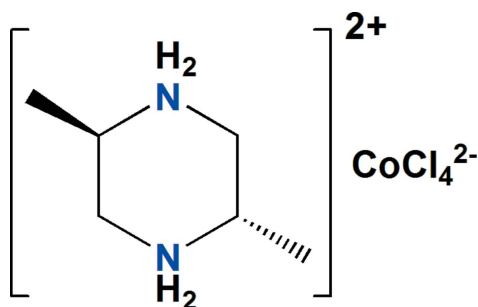
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In the title molecular salt, $(C_6H_{16}N_2)[CoCl_4]$, the complete dication is generated by crystallographic inversion symmetry and the piperazine ring adopts a chair conformation with the pendant methyl groups in equatorial orientations. The complete dianion is generated by crystallographic twofold symmetry. In the crystal, the $(C_6H_{16}N_2)^{2+}$ and $[CoCl_4]^{2-}$ ions are linked by $N-H \cdots Cl$ and $C-H \cdots Cl$ hydrogen bonds, thereby forming a two-dimensional supramolecular network. The Hirshfeld surface analysis and fingerprint plots reveal that the largest contributions to the crystal stability come from $H \cdots Cl/Cl \cdots H$ (68.4%) and $H \cdots H$ (27.4%) contacts.

1. Chemical context

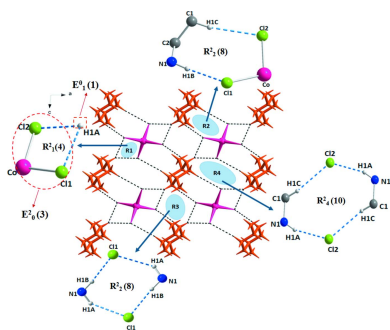
Tetrachlorocobalt/copper (II) salts with organic cations, such as $(C_6H_{10}N_3)_2[CoCl_4]$ (Titi *et al.* 2020), $[(CH_3)_2NH_2]_2[CoCl_4]$ (Pietraszko *et al.* 2006) and $(C_7H_7N_2S)_2[CuCl_4]$ (Vishwakarma *et al.* 2017) have received attention due to their potential applications in the electronic, magnetic, optical and anti-microbial fields. In these materials, the negative charge on the inorganic complex ion is balanced by the organic groups, which usually act as structure-directing agents by the formation of $N-H \cdots Cl$ hydrogen bonds and significantly affect the structure and dimensionality of the supramolecular network.



As an extension of these studies, we now describe the synthesis, structure and Hirshfeld surface analysis of the title molecular salt, (I).

2. Structural commentary

The asymmetric unit of (I) comprises half of a *trans*-2,5-dimethylpiperazine-1,4-dium cation and a half tetrachloridocobaltate anion (Fig. 1). The cation and anion are completed by crystallographic inversion and twofold symmetry, respec-



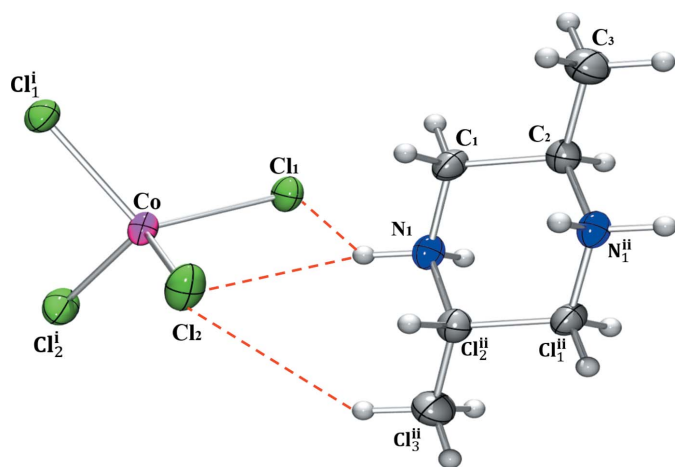


Figure 1
The molecular structure of (I) with displacement ellipsoids set to 50% probability and hydrogen bonds shown as dashed lines. Symmetry codes: (i) $-x + 1, y, -z + \frac{3}{2}$; (ii) $-x + 2, -y + 1, -z + 1$.

tively. In the organic species, the N—C and C—C bond lengths vary from 1.490 (2) to 1.513 (2) Å and the angles C—C—C, N—C—C and C—N—C range from 109.15 (14) to 113.54 (15)°. These data are in agreement with those reported in other salts of the *trans*-2,5-dimethylpiperazine-1,4-dium

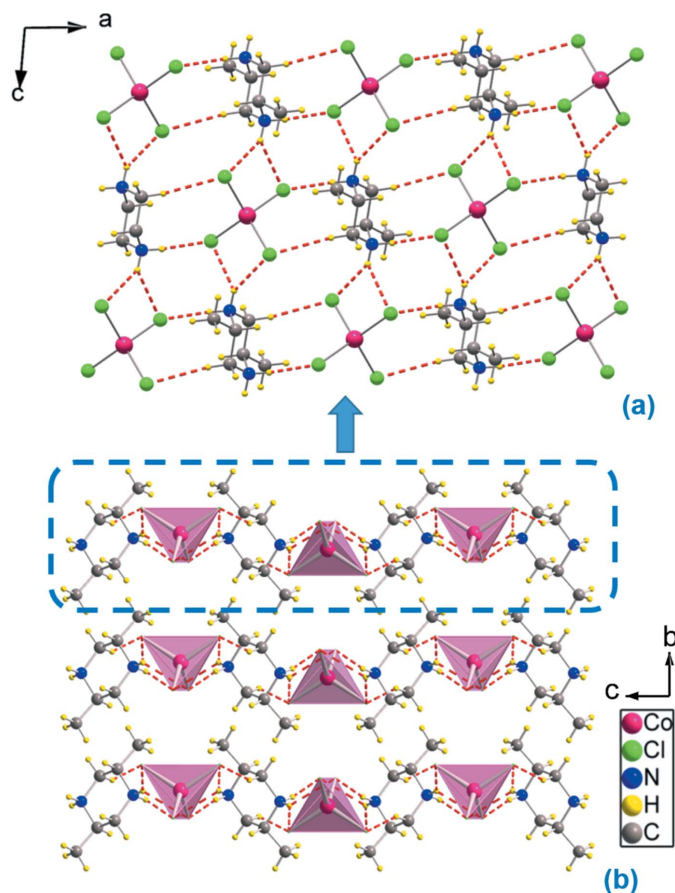


Figure 2
(a) Crystal packing in the structure of (I) along the crystallographic *a* axis. (b) View of a supramolecular layer along the *b*-axis direction.

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

<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>
N1—H1A···Cl1 ⁱ	0.89	2.30	3.1777 (2)	171
N1—H1B···Cl1	0.89	2.65	3.2594 (2)	126
N1—H1B···Cl2	0.89	2.49	3.2631 (2)	145
C1—H1C···Cl2 ⁱⁱ	0.97	2.82	3.7065 (2)	153

Symmetry codes: (i) $-x + 2, y, -z + \frac{3}{2}$; (ii) $-x + 1, -y + 1, -z + 1$.

cation (Gatfaoui *et al.*, 2014; Ben Mleh *et al.*, 2016). The Co²⁺ ion in (I) has a tetrahedral geometry, with Cl—Co—Cl angles ranging from 103.32 (2) to 116.57 (3)°. The average length of the Co—Cl bonds, 2.27 Å, is close to that observed in similar complexes (Tahenti *et al.*, 2020; Zhang *et al.*, 2005; Zeller *et al.*, 2005).

3. Supramolecular features

In the crystal of (I), adjacent anions are interconnected by the cations *via* N—H···Cl hydrogen bonds and C—H···Cl interactions (Table 1) to form a layer built up from the organic and inorganic species, lying parallel to (101) (Fig. 2). The hydrogen bonds engage the chloride ions of the [CoCl₄]²⁻ tetrahedron, producing four types of graph-set motifs on the basis of Etter's notation (Etter *et al.*, 1990; Bernstein *et al.*, 1995). The isolated molecules can be described by the elementary graph-set descriptors $E_d^a(n)$ (Daszkiewicz, 2012). The graph-set descriptor of the pattern can be easily obtained by the summation of elementary $E_d^a(n)$ graph-sets of isolated ions and molecules. In the case of (I), the elementary graph-sets can be collected (Fig. 3) as follows:

$$\begin{aligned} E_1^0(1) + E_0^2(3) &= R_1^2(4) \\ 2E_2^0(3) + 2E_0^1(1) &= R_4^2(8) \\ E_0^2(3) + E_0^2(5) &= R_2^2(8) \\ 2E_0^1(1) + 2E_2^0(4) &= R_4^2(10). \end{aligned}$$

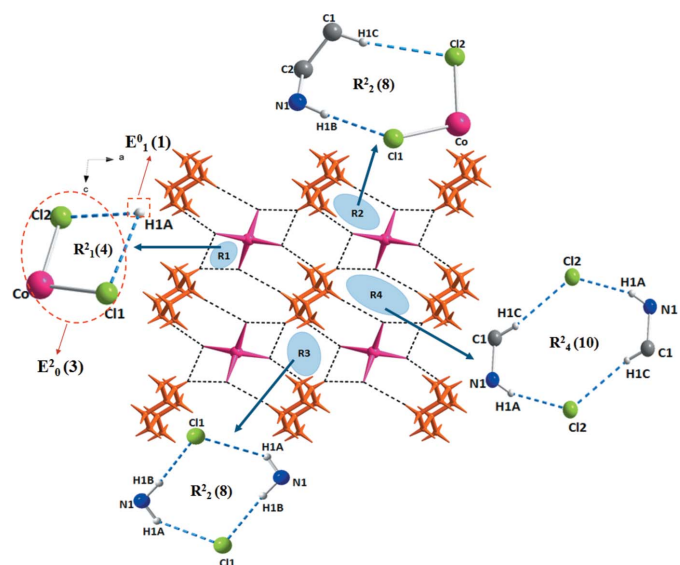


Figure 3
Hydrogen-bonding interactions between cations and anions showing the ring patterns of weak interactions formed by N—H···Cl/C—H···Cl links.

4. Hirshfeld surface analysis

To further understand the different interactions and contacts in the crystal of (I), its Hirshfeld surface (HS) (McKinnon *et al.*, 2004) was calculated. The d_{norm} surface (Fig. 4) and the associated two-dimensional fingerprint plots (see supporting information) were calculated using *CrystalExplorer 3.1* (Wolff *et al.*, 2013; Spackman & Jayatilaka, 2009). This figure shows the areas mapped in the range from -0.480 to 1.048 of the asymmetric ion-pair surrounded by neighboring ions where we can see some of the closest intermolecular contacts. The large dark-red spots on the HS indicate close contact interactions, which are primarily responsible for significant hydrogen-bond contacts. The fingerprint plots indicate that the most important interactions are $\text{H}\cdots\text{Cl}/\text{Cl}\cdots\text{H}$, which cover a HS range of 68.4% and appear as two shape-symmetric spikes in the two-dimensional fingerprint maps (where $d_i \sim d_e \sim 1.4$ Å). It should be also noted that the van der Waals radii of the hydrogen and chlorine atoms are 1.20 and 1.75 Å, respectively. The $\text{H}\cdots\text{H}$ contacts represent the second most abundant interactions with 27.4% of the total Hirshfeld surface, including a short $\text{H}\cdots\text{H}$ contact near 2.4 Å (where $d_i \sim d_e \sim 1.2$ Å), represented by a cluster of points accumulated on the diagonal of the graph. Other contacts including $\text{Cl}\cdots\text{Cl}$ and $\text{Co}\cdots\text{H}/\text{H}\cdots\text{Co}$ have negligible contributions (respectively 2.7% and 1.5%). It can be concluded that the $\text{Cl}\cdots\text{H}/\text{H}\cdots\text{Cl}$ interactions dominate in the title compound.

4.1. Synthesis and crystallization

A 1:1 mixture of *trans*-2,5-dimethylpiperazine and cobalt(II) chloride hexahydrate was dissolved in a solution of concentrated hydrochloric acid and the resulting solution was magnetically stirred for 1 h. After two weeks of evaporation, dark-blue prismatic crystals of (I) had formed, which were recovered by filtration and dried in air.

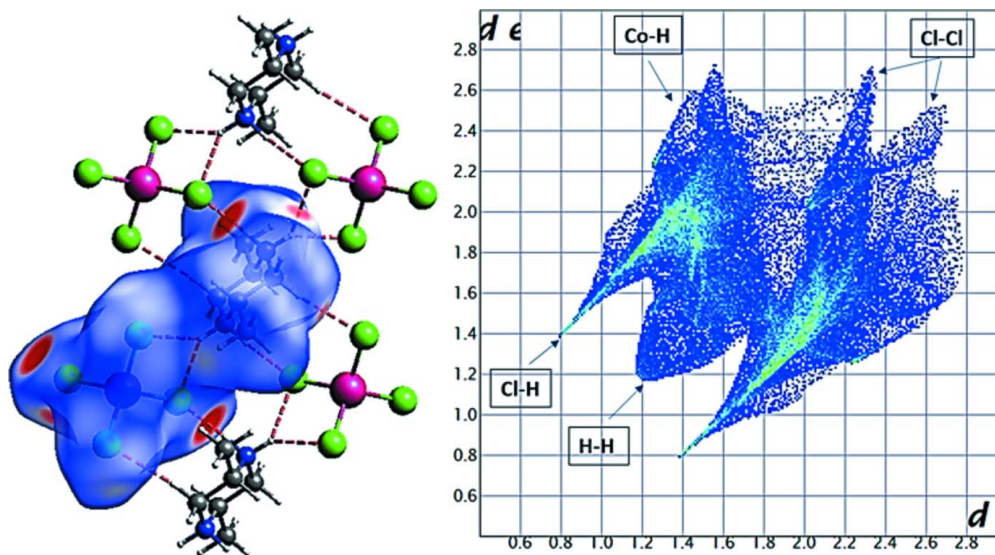


Figure 4
Hirshfeld surface of (I) mapped over d_{norm} and the two-dimensional fingerprint plot for all interactions.

Table 2
Experimental details.

Crystal data	
Chemical formula	$\text{C}_6\text{H}_{16}\text{N}_2^{2+}\cdot\text{Cl}_4\text{Co}^{2-}$
M_r	316.94
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	293
a, b, c (Å)	7.6431 (3), 11.9347 (6), 14.0058 (7)
β (°)	95.519 (4)
V (Å ³)	1271.66 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	2.15
Crystal size (mm)	0.15 × 0.10 × 0.08
Data collection	
Diffractometer	Agilent SuperNova, Single source at offset, Eos
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Agilent 2014)
$T_{\text{min}}, T_{\text{max}}$	0.816, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4627, 1546, 1370
R_{int}	0.029
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.685
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.028, 0.074, 1.08
No. of reflections	1546
No. of parameters	60
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.27, -0.59

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SIR92* (Altomare *et al.*, 1994), *SHELXL2017/1* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2006) and *ORTEP-III* (Burnett & Johnson, 1996).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The N-bound and C-bound hydrogen atoms were positioned geometrically and treated as riding atoms: $\text{N}-\text{H} = 0.86$ Å, $\text{C}-\text{H} = 0.96$ Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N,C})$.

Acknowledgements

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supporting information

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL2017/1* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2006) and *ORTEP-III* (Burnett & Johnson, 1996).

trans-2,5-Dimethylpiperazine-1,4-dium tetrachloridocobaltate(II)

Crystal data

$C_6H_{16}N_2^{2+} \cdot Cl_4Co^{2-}$
 $M_r = 316.94$
 Monoclinic, *C2/c*
 $a = 7.6431$ (3) Å
 $b = 11.9347$ (6) Å
 $c = 14.0058$ (7) Å
 $\beta = 95.519$ (4)°
 $V = 1271.66$ (10) Å³
 $Z = 4$

$F(000) = 644$
 $D_x = 1.655$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 2258 reflections
 $\theta = 4.1$ – 29.0 °
 $\mu = 2.15$ mm⁻¹
 $T = 293$ K
 Prism, blue
 $0.15 \times 0.10 \times 0.08$ mm

Data collection

Agilent SuperNova, Single source at offset, Eos diffractometer
 Detector resolution: 16.0233 pixels mm⁻¹
 ω scans
 Absorption correction: multi-scan (CrysAlisPro; Agilent 2014)
 $T_{\min} = 0.816$, $T_{\max} = 1.000$
 4627 measured reflections

1546 independent reflections
 1370 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\max} = 29.1$ °, $\theta_{\min} = 3.4$ °
 $h = -10 \rightarrow 9$
 $k = -15 \rightarrow 15$
 $l = -18 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.074$
 $S = 1.08$
 1546 reflections
 60 parameters
 0 restraints

Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 0.515P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.027$
 $\Delta\rho_{\max} = 0.27$ e Å⁻³
 $\Delta\rho_{\min} = -0.59$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.500000	0.52995 (3)	0.750000	0.02694 (13)
Cl1	0.74705 (6)	0.42227 (4)	0.77647 (3)	0.03237 (14)
Cl2	0.54849 (7)	0.62944 (5)	0.61790 (4)	0.04332 (16)
N1	0.9250 (2)	0.51194 (13)	0.58839 (11)	0.0276 (3)
H1A	1.015221	0.493869	0.630538	0.033*
H1B	0.833857	0.527625	0.621121	0.033*
C1	0.8798 (2)	0.41357 (16)	0.52524 (14)	0.0290 (4)
H1C	0.774246	0.429831	0.483440	0.035*
H1D	0.856092	0.349324	0.564406	0.035*
C2	1.0282 (2)	0.38575 (15)	0.46508 (13)	0.0272 (4)
H2	1.130901	0.361989	0.507561	0.033*
C3	0.9775 (3)	0.29268 (17)	0.39440 (16)	0.0404 (5)
H3A	0.947344	0.226813	0.428597	0.061*
H3B	0.878228	0.315843	0.351734	0.061*
H3C	1.074621	0.276353	0.358031	0.061*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.02007 (18)	0.0374 (2)	0.0236 (2)	0.000	0.00304 (14)	0.000
Cl1	0.0239 (2)	0.0401 (3)	0.0327 (3)	0.00345 (18)	0.00040 (18)	0.00462 (18)
Cl2	0.0334 (3)	0.0564 (3)	0.0408 (3)	0.0047 (2)	0.0073 (2)	0.0198 (2)
N1	0.0252 (7)	0.0368 (8)	0.0217 (8)	-0.0012 (6)	0.0072 (6)	0.0004 (6)
C1	0.0262 (9)	0.0337 (10)	0.0279 (10)	-0.0075 (7)	0.0065 (7)	-0.0013 (7)
C2	0.0253 (8)	0.0307 (9)	0.0255 (9)	0.0012 (7)	0.0023 (7)	0.0026 (7)
C3	0.0450 (11)	0.0375 (11)	0.0394 (12)	-0.0026 (9)	0.0074 (10)	-0.0076 (9)

Geometric parameters (\AA , $^\circ$)

Co1—Cl2 ⁱ	2.2588 (5)	C1—C2	1.513 (2)
Co1—Cl2	2.2588 (5)	C1—H1C	0.9700
Co1—Cl1	2.2846 (5)	C1—H1D	0.9700
Co1—Cl1 ⁱ	2.2847 (5)	C2—C3	1.513 (3)
N1—C1	1.490 (2)	C2—H2	0.9800
N1—C2 ⁱⁱ	1.494 (2)	C3—H3A	0.9600
N1—H1A	0.8900	C3—H3B	0.9600
N1—H1B	0.8900	C3—H3C	0.9600
Cl2 ⁱ —Co1—Cl2	116.57 (3)	N1—C1—H1D	109.4

C12 ⁱ —Co1—C11	111.157 (19)	C2—C1—H1D	109.4
C12—Co1—C11	103.324 (18)	H1C—C1—H1D	108.0
C12 ⁱ —Co1—C11 ⁱ	103.325 (18)	N1 ⁱⁱ —C2—C1	109.15 (14)
C12—Co1—C11 ⁱ	111.155 (19)	N1 ⁱⁱ —C2—C3	109.31 (16)
C11—Co1—C11 ⁱ	111.54 (3)	C1—C2—C3	111.50 (16)
C1—N1—C2 ⁱⁱ	113.54 (15)	N1 ⁱⁱ —C2—H2	108.9
C1—N1—H1A	108.9	C1—C2—H2	108.9
C2 ⁱⁱ —N1—H1A	108.9	C3—C2—H2	108.9
C1—N1—H1B	108.9	C2—C3—H3A	109.5
C2 ⁱⁱ —N1—H1B	108.9	C2—C3—H3B	109.5
H1A—N1—H1B	107.7	H3A—C3—H3B	109.5
N1—C1—C2	111.10 (14)	C2—C3—H3C	109.5
N1—C1—H1C	109.4	H3A—C3—H3C	109.5
C2—C1—H1C	109.4	H3B—C3—H3C	109.5
C2 ⁱⁱ —N1—C1—C2	56.5 (2)	N1—C1—C2—C3	-174.91 (16)
N1—C1—C2—N1 ⁱⁱ	-54.0 (2)		

Symmetry codes: (i) $-x+1, y, -z+3/2$; (ii) $-x+2, -y+1, -z+1$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots C11 ⁱⁱⁱ	0.89	2.30	3.1777 (2)	171
N1—H1B \cdots C11	0.89	2.65	3.2594 (2)	126
N1—H1B \cdots C12	0.89	2.49	3.2631 (2)	145
C1—H1C \cdots C12 ^{iv}	0.97	2.82	3.7065 (2)	153

Symmetry codes: (iii) $-x+2, y, -z+3/2$; (iv) $-x+1, -y+1, -z+1$.