Two polymorphs of 2,5-dichloro-3,6-bis(dibenzylamino)-*p*-hydroquinone with flexible dibenzylamino groups

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We obtained two conformational polymorphs of 2,5-dichloro-3,6-bis(dibenzylamino)-*p*-hydroquinone, $C_{34}H_{30}Cl_2N_2O_2$. Both polymorphs have an inversion centre at the centre of the hydroquinone ring ($Z' = \frac{1}{2}$), and there are no significant differences between their bond lengths and angles. The most significant structural difference in the molecular conformations was found in the rotation of the phenyl rings of the two crystallographically independent benzyl groups. The crystal structures of the polymorphs were distinguishable with respect to the arrangement of the hydroquinone rings and the packing motif of the phenyl rings that form part of the benzyl groups. The phenyl groups of one polymorph are arranged in a face-to-edge motif between adjacent molecules, with intermolecular C—H···π interactions, whereas the phenyl rings in the other polymorph form a lamellar stacking pattern with no significant intermolecular interactions. We suggest that this partial conformational difference in the molecular structures leads to the significant structural differences observed in their molecular arrangements.

1. Introduction

Polymorphism has attracted significant interest from both academic and industrial researchers in fields such as pharmaceuticals, foods and pigments, because the differences in the packing arrangements and molecular conformations of polymorphs result in different physicochemical properties in the crystalline state (Bernstein, 1987, 2002). Therefore, the understanding and prediction of the occurrence of polymorphs has been intensively studied, particularly focusing on molecular structure (Chrobak *et al.*, 2014; Sridhar *et al.*, 2015; Ibragimov *et al.*, 2016). Several structural parameters, such as hydrogen bonding and molecular flexibility, have been suggested as significant factors for polymorphism in molecular crystals (Yu *et al.*, 2000). In addition to these factors, there exist polymorphophores, consisting of a certain molecular skeleton which often adopts polymorphic forms (Lutker *et al.*, 2008; Zipp *et al.*, 2013). Our group has been involved in the systematic investigation of diaminodicyanopyrazine dyes (Matsuoka, 2000) with dibenzylamino groups as bulky and flexible substituents. We have previously reported different-coloured polymorphs exhibited by some pyrazine dyes, whose colour differences were attributed to conformational changes within the molecular crystals (Matsumoto *et al.*, 2006). We also found that weak halogen-related intermolecular interactions play an important role in the conformational polymorphism of a series of pyrazine dyes (Akune *et al.*, 2015, 2017). In this article, we report a new example of conformational poly-
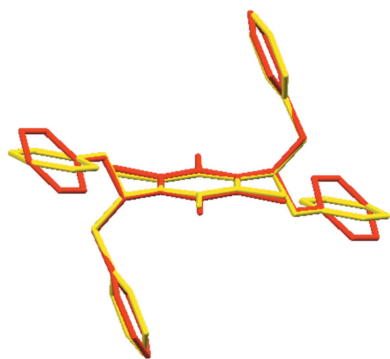
Table 1
Experimental details.

	Polymorph (**1a**)	Polymorph (**1b**)
Crystal data		
Chemical formula	$C_{34}H_{30}Cl_2N_2O_2$	$C_{34}H_{30}Cl_2N_2O_2$
M_r	569.53	569.53
Crystal system, space group	Monoclinic, $P2_1/n$	Orthorhombic, $Pbca$
Temperature (K)	296	296
a, b, c (Å)	9.67404 (18), 10.9707 (2), 13.5552 (3)	13.2054 (2), 12.4456 (2), 16.8489 (3)
α, β, γ (°)	90, 94.7380 (7), 90	90, 90, 90
V (Å^3)	1433.72 (5)	2769.09 (9)
Z	2	4
Radiation type	Cu $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	2.30	2.39
Crystal size (mm)	$0.40 \times 0.33 \times 0.23$	$0.40 \times 0.30 \times 0.29$
Data collection		
Diffractometer	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID
Absorption correction	Multi-scan (*ABSCOR*; Rigaku, 1995)	Multi-scan (*ABSCOR*; Rigaku, 1995)
T_{min}, T_{max}	0.492, 0.589	0.413, 0.507
No. of measured, independent and observed $[F^2 > 2\sigma(F^2)]$ reflections	12895, 2527, 2101	23298, 2442, 1976
R_{int}	0.070	0.039
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.595	0.595
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.125, 1.10	0.039, 0.115, 1.08
No. of reflections	2527	2442
No. of parameters	181	181
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.20, −0.32	0.24, −0.20

Computer programs: *RAPID-AUTO* (Rigaku, 2000), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2008) and *CrystalStructure* (Rigaku, 2017).

morphism of an aromatic compound having dibenzylamino groups, namely 2,5-dichloro-3,6-bis(dibenzylamino)-*p*-hydroquinone, (**1**) (see Scheme 1). We have confirmed that the dibenzylamino group plays an important role as a flexible substituent in the occurrence of polymorphism when it is attached to an aromatic moiety (Akune *et al.*, 2015).
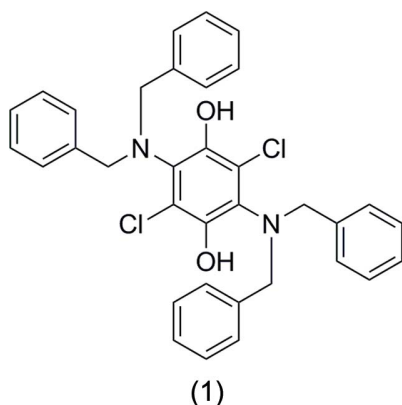
(1)
Scheme 1

2. Experimental

2.1. Synthesis and crystallization

Compound (**1**) (Fig. 1) was synthesized following the procedure reported by Shin *et al.* (2017), and its chemical structure was confirmed by conventional analytical techniques. The crystallization of (**1**) was carried out by the liquid–liquid diffusion method in a thin glass tube, using a combi-

nation of chloroform (good solvent) and methanol/ethanol (poor solvent). The crystallization samples were placed in an incubator at 288 K. Two different-coloured crystals, *i.e.* (**1a**) (pale-yellow blocks) and (**1b**) (pale-pink blocks), were obtained in the same or different tubes. Most crystals were obtained in the (**1a**) form.

However, we could also prepare significant amounts of (**1b**) by crystallization of the quinone form of (**1**), which was also carried out by liquid–liquid diffusion, using a combination of chloroform and *n*-hexane as the good and poor solvents, respectively. The quinone form of (**1**) was transformed into the hydroquinone form by ambient light during crystallization (Shin *et al.*, 2017). Thus, in contrast to the direct crystallization of (**1**), a considerable quantity of (**1b**) was obtained by this method.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were placed in

Figure 1
Photographs of (*a*) polymorph (**1a**) and (*b*) polymorph (**1b**).

geometrically idealized positions for both polymorphs, and were refined using the riding model, with C—H = 0.93 Å for aromatic H atoms, C—H = 0.97 Å for CH_2 groups and O—H = 0.82 Å for hydroxy H atoms. The H atoms were constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C,O)$ of the parent atom.

2.3. Thermal and powder X-ray diffraction (PXRD) measurements

Differential scanning calorimetry (DSC) analyses of polymorphs (**1a**) and (**1b**) were carried out using a Rigaku Thermo Plus2 DSC8230 instrument. Each polymorph (2 mg) was placed in a sealed aluminum pan with a crimped pan closure, and was analyzed against another pan containing the same amount of Al_2O_3 as the samples, which acted as the reference. The heating rate was 10 K min^{-1}. Before and after the DSC measurements, each powder sample was characterized by PXRD performed with the same equipment used for the single-crystal X-ray diffraction analysis.

3. Results and discussion

Photographs of the two polymorphs are shown in Fig. 1. The space group of (**1a**) is $P2_1/n$, with two molecules per unit cell ($Z' = \frac{1}{2}$). Polymorph (**1b**) was found to belong to the *Pbca* space group with $Z = 4$ and $Z' = 0.5$. The molecular structures of (**1a**) and (**1b**), with the atom-numbering schemes, are shown in Fig. 2. The molecules of both polymorphs were found to have an inversion centre at the centre of the hydroquinone ring. The hydroquinone rings of both polymorphs have a planar geometry and there was no significant difference between their respective bond lengths. Another similarity is that both feature intramolecular hydrogen bonds, forming five-membered rings, between the hydroxy substituents and the N atoms of the amine groups (see supporting information). Their molecular conformations also initially looked very

Table 2
Selected bond lengths (Å) for polymorphs (**1a**) and (**1b**).

Parameter	(**1a**)	(**1b**)
O1—C2	1.365 (2)	1.367 (2)
C2—C3	1.395 (3)	1.389 (3)
C1—C3	1.391 (3)	1.402 (2)
C1—C2	1.389 (3)	1.393 (2)
C3—N1	1.443 (2)	1.440 (2)
C1—Cl1	1.7309 (19)	1.7280 (19)

similar, but we found that differences in the geometry of the phenyl groups might be related to the occurrence of the polymorphs of (**1**).

Table 2 lists selected bond lengths for (**1a**) and (**1b**). The C2—O1 bond lengths are comparable to the typical C=O and C—OH bond lengths of 1.241 and 1.366 Å, and clearly indicate that the molecules in both polymorphs exist in the hydroquinone form. The C3—N1 bond lengths show that the substituted amino groups are only weakly conjugated with the central aromatic ring, in contrast to the benzoquinone form of (**1**) (Shimada *et al.*, 2015), where the length of the same C—N bond was 1.365 (4) Å. These bond lengths, and the absence of a clear bond alternation in the central ring, are additional evidence for the low extent of conjugation between the amino group and the aromatic ring. We also performed FT–IR measurements of (**1**) and its benzoquinone form. In the IR spectrum of (**1**), we observed a peak corresponding to the hydroxy group, whereas the peak corresponding to the carbonyl group was not observed in the benzoquinone form of (**1**). These results clearly indicate that (**1**) exists in the hydroquinone form.

The conformational differences between the two polymorphs depicted in Fig. 3 can also be characterized with the aid of the important angles and dihedral angles listed in Table 3. The angles around the amino groups of both polymorphs are almost the same, and their conformational differences were found to originate from the geometrical
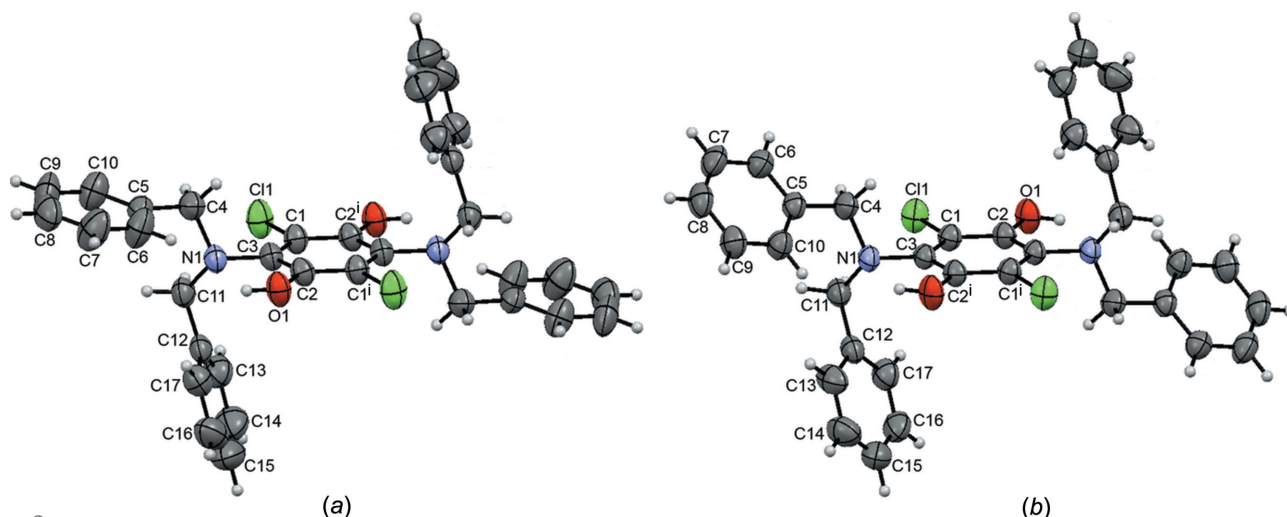

Figure 2
The molecular structures of (*a*) polymorph (**1a**) and (*b*) polymorph (**1b**), with the atom numbering. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x + 1$, $-y + 1$, $-z + 1$.]
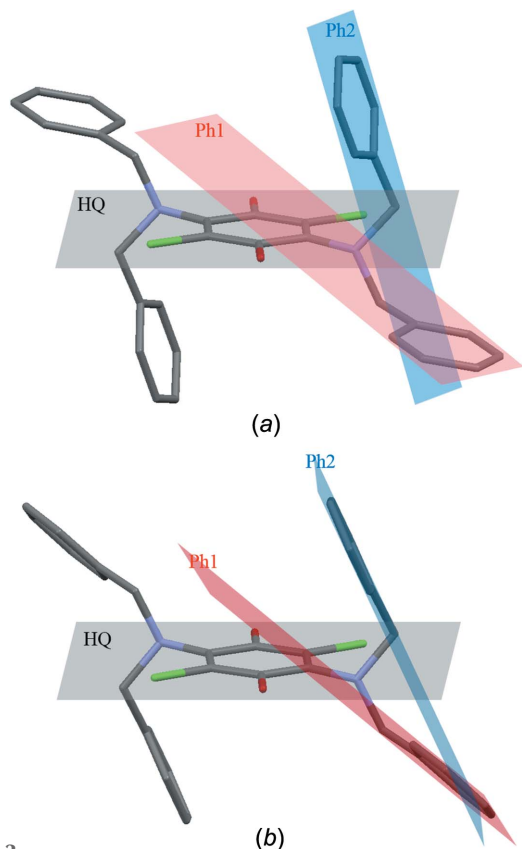
Figure 3
The molecular structures of (*a*) polymorph (**1a**) and (*b*) polymorph (**1b**), showing the calculated least-squares planes for the hydroquinone ring (HQ) and the two phenyl rings (Ph1 and Ph2).

Table 3
Parameters (°) for important angles and the dihedral angles in (**1a**) and (**1b**).

HQ, Ph1 and Ph2 are the planes of the central C1–C3/C1^i–C3^i ring, the C5–C10 phenyl ring and the C12–C17 phenyl ring, respectively [symmetry code: (i) $-x + 1, -y + 1, -z + 1$].

Parameter	(**1a**)	(**1b**)
C3—N1—C11	116.86 (15)	116.14 (13)
C3—N1—C4	112.92 (14)	112.56 (14)
N1—C4—C5	111.72 (16)	114.33 (15)
N1—C11—C12	113.74 (16)	112.48 (16)
HQ—Ph1	11.9 (2)	43.6 (2)
HQ—Ph2	74.0 (2)	65.4 (2)
Ph1—Ph2	62.12 (13)	25.63 (10)

The dihedral angles between the central hydroquinone ring and the Ph1 and Ph2 rings in (**1a**) are 11.9 (2) and 74.0 (2)°, respectively. In contrast, the corresponding dihedral angles in (**1b**) are 43.6 (2) and 65.4 (2)°. There is also a large difference in the spatial location of Ph1 with respect to the hydroquinone ring. The molecular structures of the two polymorphs suggested that the flexibility of the dibenzylamino groups contributes to the conformational variety of (**1**), similar to previous reports (Akune *et al.*, 2015, 2017). The dibenzylamino groups also affected the molecular packing structures of both polymorphs.

Fig. 4 illustrates the molecular packing structure of (**1a**). The arrangement of the hydroquinone ring between adjacent molecules is a herringbone packing motif without π–π interactions, the dihedral angle of which is around 30°. The Ph1 ring of (**1a**) is arranged in a face-to-edge motif between the Ph2 ring of adjacent molecules, with intermolecular C—H···π interactions (2.876 Å). On the other hand, the molecular packing structure of (**1b**) is significantly different from that of (**1a**) (Fig. 5). The hydroquinone rings are arranged in a zigzag

relationship of the two phenyl rings (Ph1 is atoms C5–C10 and Ph2 is C12–C17) of the respective aminobenzyl groups.
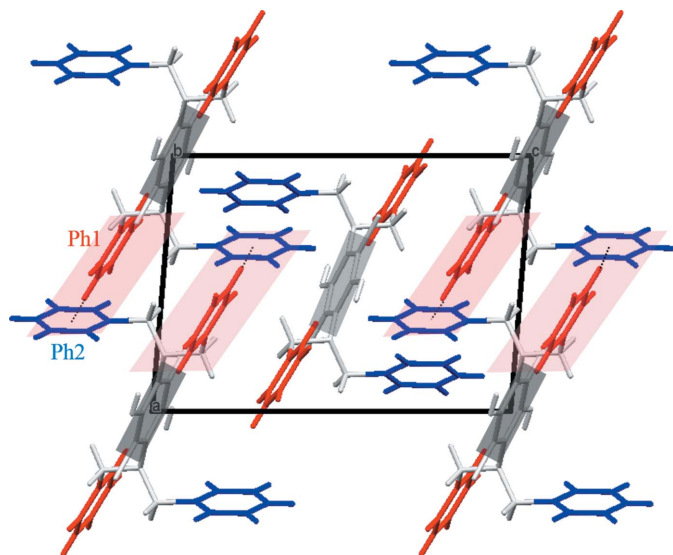

Figure 4
The molecular packing structure of polymorph (**1a**), viewed along the *b* axis, showing the hydroquinone rings in gray and the face-to-edge packing of the two neighbouring phenyl rings in pink. The dashed lines represent intermolecular C—H···π interactions between the H atoms of Ph1 and Ph2 in adjacent molecules.
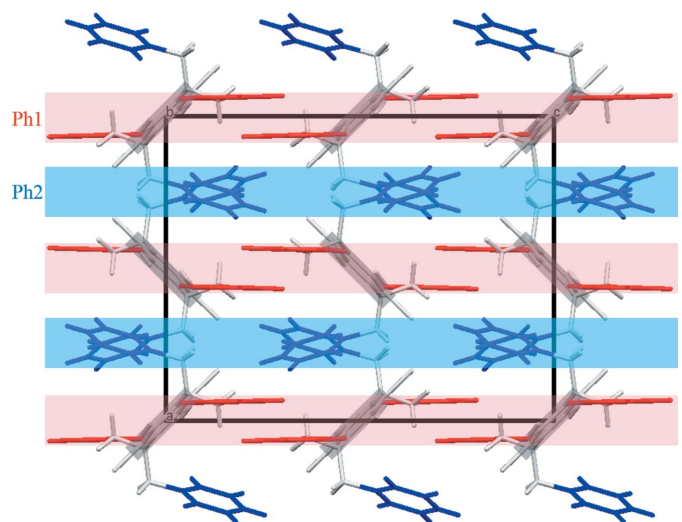

Figure 5
The molecular packing structure of polymorph (**1b**), viewed along the *b* axis. The hydroquinone rings, the lamellar stacking pattern of the Ph2 rings and the almost-parallel arrangement of the Ph1 rings to the *bc* plane are shown in gray, blue and red, respectively.

pattern along the *a* axis and the dihedral angle between them is approximately 90°. The phenyl rings were found to form a lamellar stacking pattern almost parallel to the *bc* plane, with the dihedral angles between the *bc* plane and the Ph1 and Ph2 rings being 1.38 (7) and 24.46 (8)°, respectively. No π–π interactions or significant C—H···π interactions were identified in this packing motif. We consider the slight change in the rotation of the phenyl ring in the benzyl group between the two polymorphs as contributing to the considerable structural difference in their packing motifs. This result clearly indicates that the dibenzylamino group is a parameter for the occurrence of conformational polymorphism.

DSC measurements were also carried out for the polymorphs in order to check their thermal stability. We found that both polymorphs exhibited only a single sharp peak corresponding to their melting points at 445 K for (**1a**) and 444 K for (**1b**) (see the supporting information for the DSC plots; Fig. S1). The cooled powdered samples of both polymorphs following DSC measurements were characterized to be the (**1a**) form based on their PXRD patterns (see the supporting information for the PXRD patterns; Figs. S2–S4).

4. Conclusion

Two conformational polymorphs of 2,5-dichloro-3,6-bis(dibenzylamino)-*p*-hydroquinone were obtained and their crystal structures were analyzed. A large difference in the conformation of one of the phenyl rings of the benzyl groups of the amino moiety was suggested to have contributed to the occurrence of this conformational polymorphism. These findings illustrate a new example of the presence of a dibenzylamino group attached to an aromatic moiety with the occurrence of conformational polymorphism.

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supporting information

Two polymorphs of 2,5-dichloro-3,6-bis(dibenzylamino)-*p*-hydroquinone with flexible dibenzylamino groups

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Computing details

For both structures, data collection: *RAPID-AUTO* (Rigaku, 2000); cell refinement: *RAPID-AUTO* (Rigaku, 2000); data reduction: *RAPID-AUTO* (Rigaku, 2000); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *CrystalStructure* (Rigaku, 2017) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2017).

2,5-Bis(dibenzylamino)-3,6-dichlorobenzene-1,4-diol (20130730_colorless_block)

Crystal data

$C_{34}H_{30}Cl_2N_2O_2$	$F(000) = 596.00$
$M_r = 569.53$	$D_x = 1.319$ Mg m^{-3}
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, $\lambda = 1.54187$ Å
$a = 9.67404$ (18) Å	Cell parameters from 10981 reflections
$b = 10.9707$ (2) Å	$\theta = 3.3$–$68.2°$
$c = 13.5552$ (3) Å	$\mu = 2.30$ mm^{-1}
$\beta = 94.7380$ (7)°	$T = 296$ K
$V = 1433.72$ (5) Å^3	Block, colorless
$Z = 2$	$0.40 \times 0.33 \times 0.23$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer	2527 independent reflections
Detector resolution: 10.000 pixels mm^{-1}	2101 reflections with $F^2 > 2.0\sigma(F^2)$
ω scans	$R_{int} = 0.070$
Absorption correction: multi-scan (ABSCOR; Rigaku, 1995)	$\theta_{max} = 66.5°$, $\theta_{min} = 5.2°$
$T_{min} = 0.492$, $T_{max} = 0.589$	$h = -11 \rightarrow 11$
12895 measured reflections	$k = -13 \rightarrow 12$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.042$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.125$	H-atom parameters constrained
$S = 1.10$	$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 0.3915P]$ where $P = (F_o^2 + 2F_c^2)/3$
2527 reflections	
181 parameters	$(\Delta/\sigma)_{max} < 0.001$
0 restraints	$\Delta\rho_{max} = 0.20$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.32$ 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.

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2. R-factor (gt) are based on F. The threshold expression of $F^2 > 2.0$ sigma(F^2) is used only for calculating R-factor (gt).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.23763 (5)	0.60878 (5)	0.58672 (5)	0.0671 (2)
O1	0.50864 (15)	0.25956 (12)	0.44492 (11)	0.0578 (4)
H1	0.4330	0.2280	0.4510	0.069*
N1	0.27948 (15)	0.33329 (14)	0.52062 (11)	0.0471 (4)
C1	0.38157 (19)	0.54615 (17)	0.53814 (14)	0.0472 (5)
C2	0.50464 (19)	0.37915 (16)	0.47231 (14)	0.0456 (4)
C3	0.38501 (18)	0.42424 (17)	0.51024 (14)	0.0443 (4)
C4	0.2697 (2)	0.2951 (2)	0.62473 (15)	0.0563 (5)
H4A	0.2169	0.3553	0.6582	0.068*
H4B	0.3621	0.2916	0.6584	0.068*
C5	0.2012 (2)	0.17238 (19)	0.63111 (14)	0.0511 (5)
C6	0.2621 (3)	0.0708 (2)	0.5945 (2)	0.0787 (8)
H6	0.3439	0.0794	0.5636	0.094*
C7	0.2052 (4)	−0.0436 (3)	0.6023 (2)	0.0935 (9)
H7	0.2487	−0.1109	0.5769	0.112*
C8	0.0857 (3)	−0.0581 (3)	0.6468 (2)	0.0825 (8)
H8	0.0466	−0.1351	0.6515	0.099*
C9	0.0231 (3)	0.0415 (3)	0.6847 (2)	0.0894 (9)
H9	−0.0586	0.0320	0.7155	0.107*
C10	0.0815 (3)	0.1569 (2)	0.6773 (2)	0.0747 (7)
H10	0.0389	0.2239	0.7038	0.090*
C11	0.14278 (19)	0.3557 (2)	0.46778 (15)	0.0534 (5)
H11A	0.1028	0.4281	0.4950	0.064*
H11B	0.0823	0.2876	0.4794	0.064*
C12	0.14744 (19)	0.37228 (19)	0.35847 (15)	0.0513 (5)
C13	0.1040 (3)	0.4804 (2)	0.31389 (18)	0.0696 (6)
H13	0.0771	0.5446	0.3528	0.084*
C14	0.1000 (3)	0.4945 (3)	0.2136 (2)	0.0937 (9)
H14	0.0698	0.5678	0.1848	0.112*
C15	0.1400 (3)	0.4016 (4)	0.1557 (2)	0.0994 (11)
H15	0.1376	0.4119	0.0875	0.119*
C16	0.1842 (3)	0.2922 (3)	0.1976 (2)	0.0884 (9)
H16	0.2115	0.2288	0.1580	0.106*
C17	0.1872 (2)	0.2781 (2)	0.29918 (18)	0.0653 (6)
H17	0.2164	0.2045	0.3279	0.078*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0469 (3)	0.0551 (4)	0.1018 (5)	0.0003 (2)	0.0209 (3)	−0.0140 (3)
O1	0.0512 (8)	0.0380 (7)	0.0852 (10)	−0.0062 (6)	0.0105 (7)	−0.0088 (7)
N1	0.0411 (8)	0.0449 (9)	0.0552 (9)	−0.0097 (7)	0.0031 (7)	0.0023 (7)
C1	0.0386 (9)	0.0423 (11)	0.0608 (11)	0.0005 (8)	0.0050 (8)	−0.0005 (8)
C2	0.0429 (10)	0.0369 (10)	0.0566 (11)	−0.0014 (7)	0.0023 (8)	−0.0035 (8)
C3	0.0383 (9)	0.0405 (10)	0.0539 (10)	−0.0044 (7)	0.0020 (8)	0.0012 (8)
C4	0.0623 (13)	0.0525 (12)	0.0539 (11)	−0.0106 (10)	0.0034 (9)	0.0018 (9)
C5	0.0507 (11)	0.0511 (12)	0.0513 (11)	−0.0068 (9)	0.0040 (8)	0.0062 (9)
C6	0.0799 (17)	0.0577 (15)	0.104 (2)	−0.0041 (12)	0.0393 (15)	0.0087 (13)
C7	0.121 (2)	0.0533 (16)	0.112 (2)	−0.0106 (15)	0.0447 (19)	0.0034 (14)
C8	0.0879 (19)	0.0638 (17)	0.0942 (19)	−0.0256 (15)	−0.0020 (15)	0.0164 (14)
C9	0.0590 (15)	0.094 (2)	0.117 (2)	−0.0174 (14)	0.0193 (14)	0.0338 (18)
C10	0.0664 (15)	0.0677 (16)	0.0934 (18)	0.0009 (12)	0.0275 (13)	0.0113 (13)
C11	0.0388 (10)	0.0586 (12)	0.0628 (12)	−0.0069 (9)	0.0028 (9)	0.0030 (9)
C12	0.0378 (10)	0.0537 (12)	0.0616 (12)	−0.0105 (8)	−0.0010 (8)	0.0042 (9)
C13	0.0696 (15)	0.0632 (15)	0.0751 (15)	−0.0053 (12)	0.0002 (12)	0.0099 (12)
C14	0.097 (2)	0.095 (2)	0.087 (2)	−0.0101 (18)	−0.0032 (16)	0.0305 (18)
C15	0.086 (2)	0.147 (3)	0.0642 (17)	−0.020 (2)	0.0021 (15)	0.0167 (19)
C16	0.0723 (17)	0.118 (3)	0.0746 (17)	−0.0085 (17)	0.0060 (13)	−0.0263 (17)
C17	0.0573 (13)	0.0657 (15)	0.0722 (15)	−0.0038 (11)	0.0006 (11)	−0.0074 (12)

Geometric parameters (Å, º)

Cl1—C1	1.7309 (19)	C8—C9	1.369 (4)
O1—C2	1.365 (2)	C8—H8	0.9300
O1—H1	0.8200	C9—C10	1.393 (4)
N1—C3	1.443 (2)	C9—H9	0.9300
N1—C11	1.472 (2)	C10—H10	0.9300
N1—C4	1.482 (2)	C11—C12	1.497 (3)
C1—C2^i	1.389 (3)	C11—H11A	0.9700
C1—C3	1.391 (3)	C11—H11B	0.9700
C2—C1^i	1.389 (3)	C12—C13	1.381 (3)
C2—C3	1.395 (3)	C12—C17	1.383 (3)
C4—C5	1.507 (3)	C13—C14	1.365 (4)
C4—H4A	0.9700	C13—H13	0.9300
C4—H4B	0.9700	C14—C15	1.363 (5)
C5—C10	1.372 (3)	C14—H14	0.9300
C5—C6	1.372 (3)	C15—C16	1.380 (5)
C6—C7	1.378 (4)	C15—H15	0.9300
C6—H6	0.9300	C16—C17	1.384 (4)
C7—C8	1.356 (4)	C16—H16	0.9300
C7—H7	0.9300	C17—H17	0.9300
C2—O1—H1	109.5	C8—C9—C10	120.2 (3)
C3—N1—C11	116.86 (15)	C8—C9—H9	119.9

C3—N1—C4	112.92 (14)	C10—C9—H9	119.9
C11—N1—C4	112.65 (15)	C5—C10—C9	120.5 (3)
C2ⁱ—C1—C3	120.17 (17)	C5—C10—H10	119.7
C2ⁱ—C1—Cl1	118.29 (15)	C9—C10—H10	119.7
C3—C1—Cl1	121.55 (14)	N1—C11—C12	113.74 (16)
O1—C2—C1ⁱ	119.93 (17)	N1—C11—H11A	108.8
O1—C2—C3	118.95 (17)	C12—C11—H11A	108.8
C1ⁱ—C2—C3	121.12 (17)	N1—C11—H11B	108.8
C1—C3—C2	118.71 (17)	C12—C11—H11B	108.8
C1—C3—N1	127.26 (17)	H11A—C11—H11B	107.7
C2—C3—N1	113.95 (16)	C13—C12—C17	118.5 (2)
N1—C4—C5	111.72 (16)	C13—C12—C11	120.3 (2)
N1—C4—H4A	109.3	C17—C12—C11	121.1 (2)
C5—C4—H4A	109.3	C14—C13—C12	121.1 (3)
N1—C4—H4B	109.3	C14—C13—H13	119.5
C5—C4—H4B	109.3	C12—C13—H13	119.5
H4A—C4—H4B	107.9	C15—C14—C13	120.2 (3)
C10—C5—C6	117.9 (2)	C15—C14—H14	119.9
C10—C5—C4	122.0 (2)	C13—C14—H14	119.9
C6—C5—C4	120.0 (2)	C14—C15—C16	120.4 (3)
C5—C6—C7	121.7 (2)	C14—C15—H15	119.8
C5—C6—H6	119.2	C16—C15—H15	119.8
C7—C6—H6	119.2	C15—C16—C17	119.2 (3)
C8—C7—C6	120.1 (3)	C15—C16—H16	120.4
C8—C7—H7	119.9	C17—C16—H16	120.4
C6—C7—H7	119.9	C12—C17—C16	120.7 (3)
C7—C8—C9	119.5 (3)	C12—C17—H17	119.7
C7—C8—H8	120.3	C16—C17—H17	119.7
C9—C8—H8	120.3		
C2ⁱ—C1—C3—C2	0.3 (3)	C5—C6—C7—C8	0.2 (5)
Cl1—C1—C3—C2	−179.49 (14)	C6—C7—C8—C9	−0.7 (5)
C2ⁱ—C1—C3—N1	176.67 (17)	C7—C8—C9—C10	0.2 (5)
Cl1—C1—C3—N1	−3.1 (3)	C6—C5—C10—C9	−1.1 (4)
O1—C2—C3—C1	179.93 (17)	C4—C5—C10—C9	−177.9 (2)
C1ⁱ—C2—C3—C1	−0.3 (3)	C8—C9—C10—C5	0.7 (4)
O1—C2—C3—N1	3.1 (3)	C3—N1—C11—C12	57.2 (2)
C1ⁱ—C2—C3—N1	−177.14 (17)	C4—N1—C11—C12	−169.59 (17)
C11—N1—C3—C1	61.2 (3)	N1—C11—C12—C13	−118.9 (2)
C4—N1—C3—C1	−71.9 (2)	N1—C11—C12—C17	64.9 (3)
C11—N1—C3—C2	−122.31 (19)	C17—C12—C13—C14	0.1 (3)
C4—N1—C3—C2	104.6 (2)	C11—C12—C13—C14	−176.1 (2)
C3—N1—C4—C5	−158.83 (17)	C12—C13—C14—C15	−0.5 (4)
C11—N1—C4—C5	66.1 (2)	C13—C14—C15—C16	0.4 (5)
N1—C4—C5—C10	−120.2 (2)	C14—C15—C16—C17	0.0 (5)
N1—C4—C5—C6	63.1 (3)	C13—C12—C17—C16	0.3 (3)

| C10—C5—C6—C7 | 0.7 (4) | C11—C12—C17—C16 | 176.5 (2) |
| C4—C5—C6—C7 | 177.6 (3) | C15—C16—C17—C12 | −0.3 (4) |

Symmetry code: (i) −x+1, −y+1, −z+1.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.82	2.16	2.645 (2)	118

2,5-Bis(dibenzylamino)-3,6-dichlorobenzene-1,4-diol (20130722_palered_block)

Crystal data

$C_{34}H_{30}Cl_2N_2O_2$
$M_r = 569.53$
Orthorhombic, $Pbca$
$a = 13.2054 (2)$ Å
$b = 12.4456 (2)$ Å
$c = 16.8489 (3)$ Å
$V = 2769.09 (9)$ Å^3
$Z = 4$
$F(000) = 1192.00$

$D_x = 1.366$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54187$ Å
Cell parameters from 17342 reflections
$\theta = 3.4–68.2°$
$\mu = 2.39$ mm^{-1}
$T = 296$ K
Block, pale red
$0.40 \times 0.30 \times 0.28$ mm

Data collection

Rigaku R-AXIS RAPID
diffractometer
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan
(ABSCOR; Rigaku, 1995)
$T_{min} = 0.413$, $T_{max} = 0.507$
23298 measured reflections

2442 independent reflections
1976 reflections with $F^2 > 2.0\sigma(F^2)$
$R_{int} = 0.039$
$\theta_{max} = 66.5°$, $\theta_{min} = 5.3°$
$h = -15\rightarrow15$
$k = -14\rightarrow14$
$l = -20\rightarrow20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.115$
$S = 1.08$
2442 reflections
181 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
$w = 1/[\sigma^2(F_o^2) + (0.0633P)^2 + 0.3919P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ 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.

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2. R-factor (gt) are based on F. The threshold expression of F^2 > 2.0 sigma(F^2) is used only for calculating R-factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.66299 (4)	0.47433 (4)	0.63253 (3)	0.0591 (2)
O1	0.54700 (11)	0.30198 (9)	0.56222 (9)	0.0591 (4)
H1	0.5169	0.2548	0.5378	0.071*
N1	0.59086 (11)	0.69385 (10)	0.55443 (9)	0.0442 (4)
C1	0.57303 (13)	0.49107 (13)	0.55909 (11)	0.0436 (4)
C2	0.52341 (13)	0.40005 (13)	0.53069 (11)	0.0426 (4)
C3	0.54977 (13)	0.59272 (13)	0.52829 (11)	0.0404 (4)
C4	0.55436 (16)	0.72490 (15)	0.63403 (12)	0.0534 (5)
H4A	0.5935	0.6863	0.6736	0.064*
H4B	0.4843	0.7025	0.6394	0.064*
C5	0.56120 (13)	0.84400 (14)	0.65136 (11)	0.0463 (4)
C6	0.56417 (15)	0.87817 (16)	0.72920 (12)	0.0559 (5)
H6	0.5655	0.8277	0.7699	0.067*
C7	0.56520 (17)	0.98641 (18)	0.74745 (14)	0.0663 (6)
H7	0.5671	1.0082	0.8002	0.080*
C8	0.56340 (16)	1.06209 (17)	0.68797 (15)	0.0662 (6)
H8	0.5633	1.1349	0.7004	0.079*
C9	0.56174 (16)	1.02952 (15)	0.61040 (15)	0.0601 (6)
H9	0.5618	1.0803	0.5699	0.072*
C10	0.56001 (15)	0.92137 (15)	0.59207 (13)	0.0543 (5)
H10	0.5580	0.9001	0.5392	0.065*
C11	0.70119 (14)	0.70866 (14)	0.54321 (12)	0.0515 (5)
H11A	0.7369	0.6508	0.5698	0.062*
H11B	0.7217	0.7757	0.5677	0.062*
C12	0.73094 (14)	0.71014 (13)	0.45730 (12)	0.0497 (5)
C13	0.71914 (18)	0.80139 (16)	0.41111 (15)	0.0698 (7)
H13	0.6907	0.8626	0.4335	0.084*
C14	0.7485 (2)	0.80329 (19)	0.33315 (16)	0.0790 (7)
H14	0.7399	0.8656	0.3034	0.095*
C15	0.79067 (18)	0.71382 (19)	0.29857 (14)	0.0718 (7)
H15	0.8106	0.7152	0.2457	0.086*
C16	0.80286 (17)	0.62302 (19)	0.34285 (15)	0.0689 (6)
H16	0.8316	0.5622	0.3200	0.083*
C17	0.77298 (16)	0.62081 (16)	0.42091 (14)	0.0609 (6)
H17	0.7812	0.5579	0.4500	0.073*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0653 (4)	0.0469 (3)	0.0651 (4)	0.0030 (2)	−0.0185 (2)	0.0012 (2)
O1	0.0731 (9)	0.0293 (6)	0.0748 (10)	0.0011 (6)	−0.0143 (7)	0.0051 (6)
N1	0.0484 (9)	0.0320 (7)	0.0523 (9)	−0.0043 (6)	0.0044 (7)	−0.0072 (6)
C1	0.0475 (10)	0.0361 (9)	0.0472 (11)	0.0015 (7)	−0.0018 (8)	−0.0018 (8)
C2	0.0497 (10)	0.0293 (8)	0.0488 (11)	0.0029 (7)	0.0014 (8)	0.0015 (7)
C3	0.0448 (9)	0.0303 (8)	0.0461 (10)	−0.0006 (7)	0.0037 (8)	−0.0030 (7)

C4	0.0672 (13)	0.0384 (10)	0.0546 (12)	−0.0027 (9)	0.0083 (9)	−0.0064 (8)
C5	0.0478 (10)	0.0376 (10)	0.0534 (11)	0.0008 (8)	0.0010 (8)	−0.0071 (8)
C6	0.0621 (12)	0.0518 (11)	0.0537 (12)	−0.0002 (9)	0.0009 (9)	−0.0068 (9)
C7	0.0749 (14)	0.0604 (13)	0.0637 (16)	−0.0002 (11)	0.0003 (11)	−0.0239 (11)
C8	0.0678 (14)	0.0420 (11)	0.0888 (17)	0.0004 (10)	−0.0005 (12)	−0.0189 (12)
C9	0.0671 (14)	0.0389 (11)	0.0744 (16)	0.0021 (9)	−0.0025 (11)	−0.0023 (10)
C10	0.0635 (13)	0.0431 (11)	0.0564 (12)	−0.0002 (9)	−0.0032 (10)	−0.0061 (9)
C11	0.0492 (11)	0.0435 (10)	0.0619 (13)	−0.0062 (8)	0.0030 (9)	−0.0064 (9)
C12	0.0455 (11)	0.0384 (9)	0.0651 (13)	−0.0057 (7)	0.0057 (9)	−0.0060 (9)
C13	0.0837 (16)	0.0427 (11)	0.0831 (17)	0.0026 (10)	0.0273 (13)	0.0010 (10)
C14	0.0929 (18)	0.0616 (14)	0.0824 (17)	−0.0039 (12)	0.0206 (15)	0.0147 (13)
C15	0.0717 (15)	0.0784 (17)	0.0653 (15)	−0.0159 (12)	0.0136 (12)	−0.0100 (13)
C16	0.0688 (14)	0.0613 (14)	0.0768 (17)	−0.0043 (11)	0.0125 (12)	−0.0224 (12)
C17	0.0637 (13)	0.0453 (11)	0.0738 (15)	0.0015 (9)	0.0048 (11)	−0.0072 (10)

Geometric parameters (Å, º)

Cl1—C1	1.7280 (19)	C8—C9	1.368 (3)
O1—C2	1.367 (2)	C8—H8	0.9300
O1—H1	0.8200	C9—C10	1.381 (3)
N1—C3	1.440 (2)	C9—H9	0.9300
N1—C4	1.477 (2)	C10—H10	0.9300
N1—C11	1.481 (2)	C11—C12	1.500 (3)
C1—C2	1.393 (2)	C11—H11A	0.9700
C1—C3	1.402 (2)	C11—H11B	0.9700
C2—C3ⁱ	1.389 (3)	C12—C13	1.385 (3)
C3—C2ⁱ	1.389 (3)	C12—C17	1.386 (3)
C4—C5	1.514 (2)	C13—C14	1.370 (3)
C4—H4A	0.9700	C13—H13	0.9300
C4—H4B	0.9700	C14—C15	1.374 (3)
C5—C6	1.379 (3)	C14—H14	0.9300
C5—C10	1.388 (3)	C15—C16	1.364 (3)
C6—C7	1.382 (3)	C15—H15	0.9300
C6—H6	0.9300	C16—C17	1.373 (3)
C7—C8	1.376 (3)	C16—H16	0.9300
C7—H7	0.9300	C17—H17	0.9300
C2—O1—H1	109.5	C8—C9—C10	120.2 (2)
C3—N1—C4	112.56 (14)	C8—C9—H9	119.9
C3—N1—C11	116.14 (13)	C10—C9—H9	119.9
C4—N1—C11	113.86 (15)	C9—C10—C5	121.00 (19)
C2—C1—C3	120.24 (17)	C9—C10—H10	119.5
C2—C1—Cl1	118.11 (13)	C5—C10—H10	119.5
C3—C1—Cl1	121.65 (13)	N1—C11—C12	112.48 (16)
O1—C2—C3ⁱ	119.62 (15)	N1—C11—H11A	109.1
O1—C2—C1	119.03 (16)	C12—C11—H11A	109.1
C3ⁱ—C2—C1	121.35 (15)	N1—C11—H11B	109.1
C2ⁱ—C3—C1	118.41 (15)	C12—C11—H11B	109.1

C2ⁱ—C3—N1	115.12 (14)	H11A—C11—H11B	107.8
C1—C3—N1	126.39 (16)	C13—C12—C17	117.0 (2)
N1—C4—C5	114.33 (15)	C13—C12—C11	121.51 (17)
N1—C4—H4A	108.7	C17—C12—C11	121.47 (17)
C5—C4—H4A	108.7	C14—C13—C12	121.4 (2)
N1—C4—H4B	108.7	C14—C13—H13	119.3
C5—C4—H4B	108.7	C12—C13—H13	119.3
H4A—C4—H4B	107.6	C13—C14—C15	120.5 (2)
C6—C5—C10	118.10 (18)	C13—C14—H14	119.8
C6—C5—C4	119.15 (17)	C15—C14—H14	119.8
C10—C5—C4	122.69 (17)	C16—C15—C14	119.2 (2)
C5—C6—C7	120.8 (2)	C16—C15—H15	120.4
C5—C6—H6	119.6	C14—C15—H15	120.4
C7—C6—H6	119.6	C15—C16—C17	120.4 (2)
C8—C7—C6	120.3 (2)	C15—C16—H16	119.8
C8—C7—H7	119.8	C17—C16—H16	119.8
C6—C7—H7	119.8	C16—C17—C12	121.5 (2)
C9—C8—C7	119.6 (2)	C16—C17—H17	119.2
C9—C8—H8	120.2	C12—C17—H17	119.2
C7—C8—H8	120.2		
C3—C1—C2—O1	−179.49 (16)	C5—C6—C7—C8	−0.1 (3)
Cl1—C1—C2—O1	0.5 (2)	C6—C7—C8—C9	−0.7 (3)
C3—C1—C2—C3ⁱ	0.0 (3)	C7—C8—C9—C10	1.2 (3)
Cl1—C1—C2—C3ⁱ	−179.99 (14)	C8—C9—C10—C5	−0.8 (3)
C2—C1—C3—C2ⁱ	0.0 (3)	C6—C5—C10—C9	0.0 (3)
Cl1—C1—C3—C2ⁱ	179.99 (14)	C4—C5—C10—C9	177.01 (19)
C2—C1—C3—N1	176.65 (16)	C3—N1—C11—C12	64.7 (2)
Cl1—C1—C3—N1	−3.4 (3)	C4—N1—C11—C12	−162.09 (15)
C4—N1—C3—C2ⁱ	106.89 (19)	N1—C11—C12—C13	80.0 (2)
C11—N1—C3—C2ⁱ	−119.33 (17)	N1—C11—C12—C17	−101.1 (2)
C4—N1—C3—C1	−69.8 (2)	C17—C12—C13—C14	−0.5 (3)
C11—N1—C3—C1	63.9 (2)	C11—C12—C13—C14	178.5 (2)
C3—N1—C4—C5	−157.91 (16)	C12—C13—C14—C15	0.1 (4)
C11—N1—C4—C5	67.2 (2)	C13—C14—C15—C16	0.0 (4)
N1—C4—C5—C6	−157.34 (17)	C14—C15—C16—C17	0.3 (4)
N1—C4—C5—C10	25.7 (3)	C15—C16—C17—C12	−0.8 (3)
C10—C5—C6—C7	0.4 (3)	C13—C12—C17—C16	0.8 (3)
C4—C5—C6—C7	−176.68 (19)	C11—C12—C17—C16	−178.1 (2)

Symmetry code: (i) −x+1, −y+1, −z+1.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1ⁱ	0.82	2.20	2.680 (2)	117

Symmetry code: (i) −x+1, −y+1, −z+1.