Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-[(2,4-Dichlorophenyl)iminomethyl]-2-hydroxy-5-methylbenzaldehyde

Işın Kılıç,[a]* Şamil Işık,[a] Erbil Ağar[b] and Ferda Erşahin[b]

[a]Department of Physics, Faculty of Arts and Science, Ondokuz Mayıs University, TR-55139 Kurupelit-Samsun, Turkey, and [b]Department of Chemistry, Faculty of Arts and Science, Ondokuz Mayıs University, 55139 Samsun, Turkey
Correspondence e-mail: ikilic@omu.edu.tr

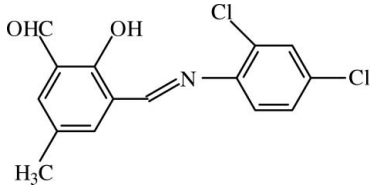
Received 14 May 2009; accepted 14 May 2009

Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.007 Å; R factor = 0.063; wR factor = 0.138; data-to-parameter ratio = 14.3.

The title compound, $C_{15}H_{11}Cl_2NO_2$, is a Schiff base which adopts the phenol–imine tautomeric form in the solid state, being stabilized by a strong intramolecular O—H···N hydrogen bond. The molecule is almost planar (r.m.s. deviation for all non-H atoms = 0.049 Å), displaying a dihedral angle of 3.1 (3)° between the planes of the two aromatic rings.

Related literature

For Schiff bases as substrates in the preparation of number of biologically active compounds, see: Siddiqui *et al.* (2006). For photochromism and thermochromism in these compounds, see: Hadjoudis *et al.* (1987); Xu *et al.* (1994). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For related structures, see: Gül *et al.* (2007) Koşar *et al.* (2005).



Experimental

Crystal data

$C_{15}H_{11}Cl_2NO_2$
M_r = 308.15
Monoclinic, $P2_1/c$
a = 19.424 (2) Å
b = 4.6113 (3) Å
c = 15.4245 (14) Å
β = 103.946 (8)°
V = 1340.9 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.48 mm^{-1}
T = 296 K
0.80 × 0.31 × 0.02 mm

Data collection

Stoe IPDS II diffractometer
Absorption correction: integration (*X-RED*; Stoe & Cie, 2002)
T_{min} = 0.817, T_{max} = 0.982
5912 measured reflections
2613 independent reflections
1228 reflections with $I > 2\sigma(I)$
R_{int} = 0.099

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.138
S = 0.91
2613 reflections
183 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.82	1.85	2.577 (4)	147

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDS II diffractometer (purchased under grant No. F279 of the University Research Fund).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2960).

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supporting information

Acta Cryst. (2009). E**65**, o1347 [doi:10.1107/S1600536809018303]

3-[(2,4-Dichlorophenyl)iminomethyl]-2-hydroxy-5-methylbenzaldehyde

Işın Kılıç, Şamil Işık, Erbil Ağar and Ferda Erşahin

S1. Comment

In this paper, a new Schiff base, (I), $C_{15}H_{11}Cl_2O_2N$ is prepared and its crystal structure is reported.

Schiff bases are synthesized from an aromatic amine and a carbonyl compound by a nucleophilic addition reaction. They are used as substrates in the preparation of number of biologically active compounds (Siddiqui *et al.*, 2006). Photochromism and thermochromism are also characteristics of these materials and arise *via* H-atom transfer from the hydroxy O atom to the N atom (Hadjoudis *et al.*, 1987; Xu *et al.*, 1994). These are two types of intra molecular hydrogen bonds in Schiff bases, in keto-amine (N—H···O) and phenol-imine (N···H—O) tautomeric forms. Our X-ray investigation shows that the title compound, (I), exists in the phenol-imine form.

An *ORTEP* view of the molecule of (I) is shown in Fig. 1. There is a strong O···N type intramolecular hydrogen bond and this intramolecular hydrogen bond (O1—H1···N1) can be described as an S(6) motif (Bernstein *et al.*, 1995). The C1—O1 [1.354 (6) Å] and C7=N1 [1.272 (6) Å] bond lengths verify the enol-imine form of (I), and these distances are agree with the corresponding distances in (*E*)-2-[4-(Dimethylamino)phenyliminomethyl]-6-methylphenol [1.350 (3) and 1.280 (2) Å; Gül *et al.*, 2007)] and in (*E*)-4-Methoxy-2- [(4-nitrophenyl)iminomethyl]phenol [1.351 (2) and 1.277 (2) Å; Koşar *et al.*, 2005]. The molecule is almost planar and the dihedral angle between the rings formed by atoms C1—C6 and C8—C13 is 3.12(0.28)°.

S2. Experimental

The compound 3-[(2,4-Dichlorophenyl)imino]methyl-2-hydroxy-5- methylbenzaldehyde was prepared by reflux a mixture of a solution containing 2-Hydroxy-5-methyl-1,3-benzenedicarboxaldehyde (0.05 g 0.3 mmol) in 20 ml e thanol and a solution containing 2,4-Dichloroaniline(0.049 g 0.3 mmol) in 20 ml e thanol. The reaction mixture was stirred for 1 hunder reflux. The crystals of 3-[(2,4-Dichlorophenyl)imino]methyl-2-hydroxy-5- methylbenzaldehyde suitable for X-ray analysis were obtained from ethylalcohol by slow evaporation (yield % 79; m.p.483–485 K).

S3. Refinement

All H atoms bound to carbon were refined using a riding model with C—H= 0.93Å and 0.96 Å $U_{iso}(H) = 1.2U_{eq}(C_{aromatic})$ and C—H= 0.96Å $U_{iso}(H) = 1.5U_{eq}(C_{methyl})$. The H atom of hydroxyl O atom was refined with O—H= 0.82Å $U_{iso}(H) = 1.5U_{eq}(O)$.

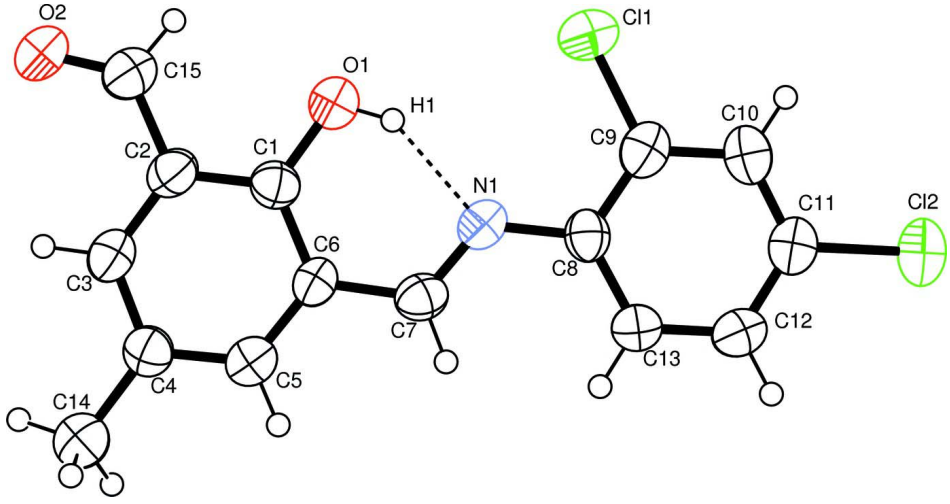

Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Dashed lines indicate intramolecular hydrogen bond.

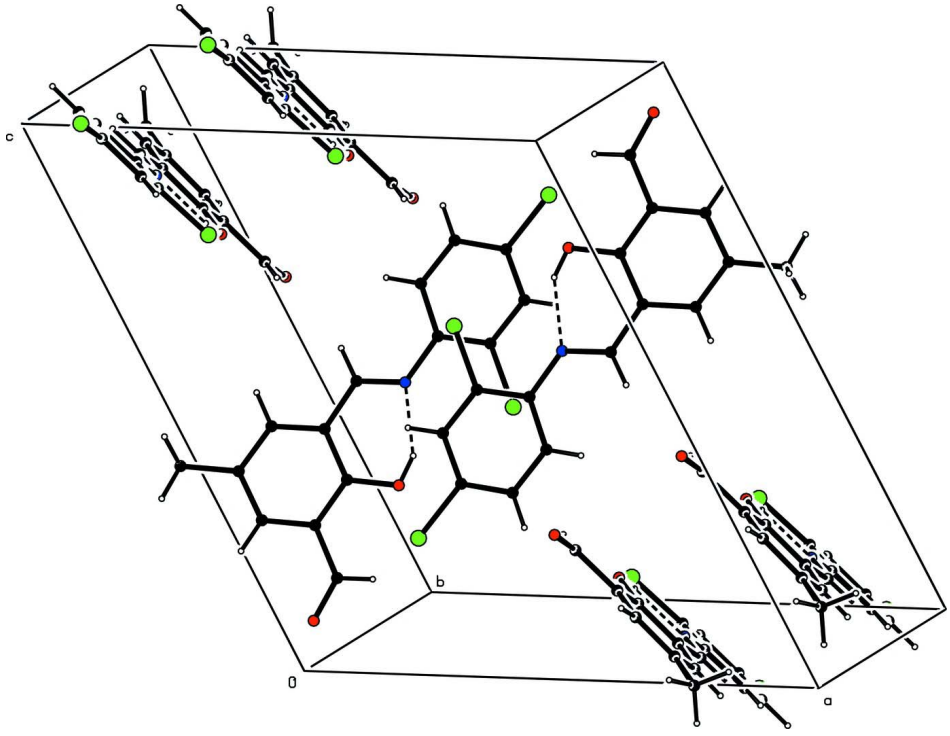

Figure 2

The crystal packing of compound (I). Dashed lines indicate intramolecular hydrogen bond.

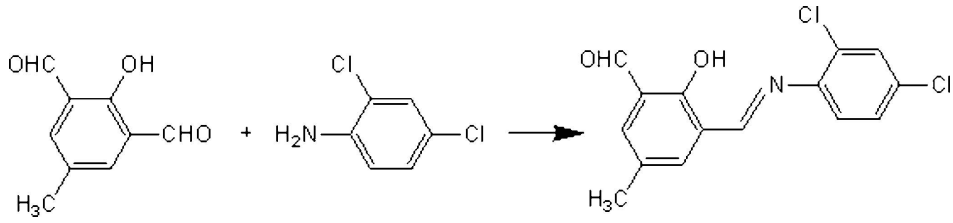

Figure 3

Synthetic scheme for $C_{15}H_{11}Cl_2O_2N$.

3-[(2,4-Dichlorophenyl)iminomethyl]-2-hydroxy-5-methylbenzaldehyde

Crystal data

$C_{15}H_{11}Cl_2NO_2$
$M_r = 308.15$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 19.424$ (2) Å
$b = 4.6113$ (3) Å
$c = 15.4245$ (14) Å
$\beta = 103.946$ (8)°
$V = 1340.9$ (2) Å^3
$Z = 4$
$F(000) = 632$
$D_x = 1.526$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6202 reflections
$\theta = 1.9$–$29.5°$
$\mu = 0.48$ mm^{-1}
$T = 296$ K
Plate, red
0.80 × 0.31 × 0.02 mm

Data collection

Stoe IPDS II diffractometer
Radiation source: fine-focus sealed tube
Plane graphite monochromator
Detector resolution: 6.67 pixels mm^{-1}
rotation method scans
Absorption correction: integration (*X-RED*; Stoe & Cie, 2002)
$T_{min} = 0.817$, $T_{max} = 0.982$
5912 measured reflections
2613 independent reflections
1228 reflections with $I > 2\sigma(I)$
$R_{int} = 0.099$
$\theta_{max} = 26.0°$, $\theta_{min} = 2.2°$
$h = -23 \rightarrow 22$
$k = -5 \rightarrow 5$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.138$
$S = 0.91$
2613 reflections
183 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Special details

Experimental. 120 frames, detector distance = 100 mm

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}
C1	0.1925 (3)	0.2637 (10)	0.3175 (3)	0.0447 (12)
C2	0.1516 (3)	0.0564 (11)	0.2629 (3)	0.0489 (12)
C3	0.0969 (3)	−0.0806 (10)	0.2900 (3)	0.0495 (13)
H3	0.0702	−0.2192	0.2528	0.059*
C4	0.0806 (2)	−0.0190 (10)	0.3702 (3)	0.0467 (12)
C5	0.1227 (2)	0.1889 (10)	0.4239 (3)	0.0472 (12)
H5	0.1134	0.2321	0.4789	0.057*
C6	0.1770 (2)	0.3330 (9)	0.3998 (3)	0.0410 (11)
C7	0.2183 (3)	0.5467 (10)	0.4580 (3)	0.0463 (12)
H7	0.2062	0.5931	0.5110	0.056*
C8	0.3140 (2)	0.8812 (9)	0.4948 (3)	0.0435 (11)
C9	0.3702 (3)	1.0022 (10)	0.4659 (3)	0.0493 (13)
C10	0.4154 (3)	1.2028 (10)	0.5178 (3)	0.0538 (14)
H10	0.4531	1.2807	0.4980	0.065*
C11	0.4039 (3)	1.2842 (10)	0.5983 (3)	0.0496 (13)
C12	0.3487 (3)	1.1723 (10)	0.6292 (3)	0.0508 (13)
H12	0.3419	1.2297	0.6843	0.061*
C13	0.3035 (3)	0.9738 (10)	0.5774 (3)	0.0500 (13)
H13	0.2656	0.9003	0.5976	0.060*
C14	0.0213 (3)	−0.1709 (12)	0.3997 (3)	0.0618 (15)
H14A	−0.0188	−0.0434	0.3918	0.093*
H14B	0.0370	−0.2233	0.4615	0.093*
H14C	0.0079	−0.3426	0.3644	0.093*
C15	0.1671 (3)	−0.0215 (13)	0.1781 (3)	0.0676 (16)
H15	0.2055	0.0712	0.1638	0.081*
Cl1	0.38664 (8)	0.8931 (3)	0.36584 (9)	0.0671 (5)
Cl2	0.46096 (7)	1.5343 (3)	0.66358 (9)	0.0634 (5)
N1	0.2710 (2)	0.6740 (8)	0.4391 (2)	0.0464 (10)
O1	0.24635 (18)	0.3927 (7)	0.2904 (2)	0.0581 (10)
H1	0.2660	0.5101	0.3282	0.087*
O2	0.1350 (2)	−0.1956 (9)	0.1242 (2)	0.0785 (12)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.046 (3)	0.044 (3)	0.045 (3)	0.000 (2)	0.012 (2)	0.003 (2)
C2	0.051 (3)	0.056 (3)	0.039 (2)	0.002 (3)	0.010 (2)	−0.004 (2)
C3	0.055 (3)	0.050 (3)	0.041 (3)	−0.002 (2)	0.006 (2)	−0.005 (2)
C4	0.043 (3)	0.047 (3)	0.048 (3)	0.003 (2)	0.009 (2)	0.000 (2)
C5	0.050 (3)	0.049 (3)	0.042 (2)	0.005 (2)	0.010 (2)	−0.001 (2)

C6	0.047 (3)	0.037 (3)	0.037 (2)	0.001 (2)	0.006 (2)	−0.003 (2)
C7	0.055 (3)	0.044 (3)	0.041 (2)	0.005 (3)	0.015 (2)	0.004 (2)
C8	0.045 (3)	0.037 (3)	0.046 (3)	−0.001 (2)	0.005 (2)	0.002 (2)
C9	0.057 (3)	0.041 (3)	0.046 (3)	0.005 (3)	0.004 (2)	0.000 (2)
C10	0.052 (3)	0.045 (3)	0.061 (3)	−0.005 (2)	0.008 (3)	0.000 (2)
C11	0.052 (3)	0.043 (3)	0.049 (3)	0.003 (2)	0.002 (2)	0.001 (2)
C12	0.058 (3)	0.052 (3)	0.045 (3)	0.005 (3)	0.017 (2)	−0.001 (2)
C13	0.053 (3)	0.055 (3)	0.044 (3)	−0.006 (3)	0.017 (2)	−0.003 (2)
C14	0.063 (3)	0.062 (4)	0.062 (3)	−0.003 (3)	0.018 (3)	−0.007 (3)
C15	0.063 (3)	0.089 (4)	0.054 (3)	−0.012 (3)	0.021 (3)	−0.018 (3)
Cl1	0.0730 (9)	0.0789 (10)	0.0548 (7)	−0.0040 (8)	0.0263 (7)	−0.0082 (7)
Cl2	0.0617 (8)	0.0510 (8)	0.0691 (8)	−0.0052 (7)	−0.0007 (7)	−0.0080 (7)
N1	0.053 (2)	0.046 (2)	0.039 (2)	0.003 (2)	0.0093 (19)	−0.0035 (18)
O1	0.061 (2)	0.063 (2)	0.0516 (19)	−0.0117 (18)	0.0160 (17)	−0.0102 (17)
O2	0.086 (3)	0.101 (3)	0.052 (2)	−0.028 (2)	0.023 (2)	−0.026 (2)

Geometric parameters (Å, º)

C1—O1	1.354 (6)	C8—N1	1.416 (5)
C1—C2	1.390 (6)	C9—C10	1.390 (6)
C1—C6	1.411 (7)	C9—Cl1	1.725 (5)
C2—C3	1.384 (7)	C10—C11	1.366 (7)
C2—C15	1.457 (7)	C10—H10	0.9300
C3—C4	1.378 (7)	C11—C12	1.374 (7)
C3—H3	0.9300	C11—Cl2	1.742 (5)
C4—C5	1.395 (6)	C12—C13	1.382 (6)
C4—C14	1.510 (7)	C12—H12	0.9300
C5—C6	1.371 (6)	C13—H13	0.9300
C5—H5	0.9300	C14—H14A	0.9600
C6—C7	1.440 (6)	C14—H14B	0.9600
C7—N1	1.272 (6)	C14—H14C	0.9600
C7—H7	0.9300	C15—O2	1.215 (5)
C8—C9	1.391 (7)	C15—H15	0.9300
C8—C13	1.404 (7)	O1—H1	0.8200
O1—C1—C2	119.2 (4)	C10—C9—Cl1	118.8 (4)
O1—C1—C6	121.8 (4)	C8—C9—Cl1	119.9 (4)
C2—C1—C6	119.1 (5)	C11—C10—C9	119.2 (5)
C3—C2—C1	120.0 (4)	C11—C10—H10	120.4
C3—C2—C15	120.0 (4)	C9—C10—H10	120.4
C1—C2—C15	120.0 (5)	C10—C11—C12	121.6 (5)
C4—C3—C2	122.4 (4)	C10—C11—Cl2	119.1 (4)
C4—C3—H3	118.8	C12—C11—Cl2	119.3 (4)
C2—C3—H3	118.8	C11—C12—C13	119.3 (5)
C3—C4—C5	116.5 (5)	C11—C12—H12	120.4
C3—C4—C14	122.1 (4)	C13—C12—H12	120.4
C5—C4—C14	121.4 (5)	C12—C13—C8	120.9 (5)
C6—C5—C4	123.4 (5)	C12—C13—H13	119.5

C6—C5—H5	118.3	C8—C13—H13	119.5
C4—C5—H5	118.3	C4—C14—H14A	109.5
C5—C6—C1	118.6 (4)	C4—C14—H14B	109.5
C5—C6—C7	120.8 (4)	H14A—C14—H14B	109.5
C1—C6—C7	120.5 (5)	C4—C14—H14C	109.5
N1—C7—C6	122.1 (5)	H14A—C14—H14C	109.5
N1—C7—H7	118.9	H14B—C14—H14C	109.5
C6—C7—H7	118.9	O2—C15—C2	126.4 (5)
C9—C8—C13	117.8 (4)	O2—C15—H15	116.8
C9—C8—N1	118.0 (4)	C2—C15—H15	116.8
C13—C8—N1	124.2 (5)	C7—N1—C8	124.2 (4)
C10—C9—C8	121.2 (5)	C1—O1—H1	109.5

O1—C1—C2—C3	179.1 (4)	C13—C8—C9—C10	1.5 (7)
C6—C1—C2—C3	−0.6 (7)	N1—C8—C9—C10	−178.8 (4)
O1—C1—C2—C15	0.5 (7)	C13—C8—C9—Cl1	179.0 (3)
C6—C1—C2—C15	−179.2 (4)	N1—C8—C9—Cl1	−1.3 (6)
C1—C2—C3—C4	0.2 (7)	C8—C9—C10—C11	−0.7 (7)
C15—C2—C3—C4	178.9 (4)	Cl1—C9—C10—C11	−178.2 (4)
C2—C3—C4—C5	−0.5 (7)	C9—C10—C11—C12	0.0 (7)
C2—C3—C4—C14	−179.5 (4)	C9—C10—C11—Cl2	179.7 (3)
C3—C4—C5—C6	1.2 (7)	C10—C11—C12—C13	−0.3 (7)
C14—C4—C5—C6	−179.8 (4)	Cl2—C11—C12—C13	−180.0 (4)
C4—C5—C6—C1	−1.5 (7)	C11—C12—C13—C8	1.2 (7)
C4—C5—C6—C7	179.7 (4)	C9—C8—C13—C12	−1.8 (7)
O1—C1—C6—C5	−178.5 (4)	N1—C8—C13—C12	178.5 (4)
C2—C1—C6—C5	1.2 (6)	C3—C2—C15—O2	2.4 (9)
O1—C1—C6—C7	0.3 (7)	C1—C2—C15—O2	−179.0 (5)
C2—C1—C6—C7	180.0 (4)	C6—C7—N1—C8	−178.7 (4)
C5—C6—C7—N1	176.8 (4)	C9—C8—N1—C7	179.7 (4)
C1—C6—C7—N1	−2.0 (7)	C13—C8—N1—C7	−0.6 (7)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.82	1.85	2.577 (4)	147