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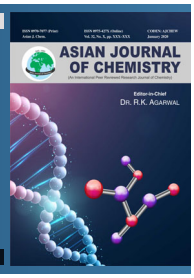

Synthesis, Characterization, Crystallographic Studies of 5-Acetyl-8-hydroxyquinoline and Their Chalcone Derivatives

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An efficient, easy and one pot synthesis for the Friedel-Craft acetylation reaction of quinolines was developed. The reaction between 8-hydroxyquinoline and acetyl/benzoyl chloride in nitrobenzene immediately flocculates as yellow precipitate. On further addition of Lewis acid causes the Friedel-Craft acetylation leads to formation of acetylated quionlines in good yields. The structure of compound 5-acetyl-8-hydroxyquinoline (**3**) was confirmed by single crystal X-ray diffraction studies. The compound crystallizes in the monoclinic crystal system with the space group $P2_1/c$. The synthesized acetylated quionlines undergoes condensation reaction with aromatic aldehydes leads to 8-hydroxyquinoline chalcones derivatives. The products were characterized by spectral studies, elemental analysis and single crystal X-ray diffraction studies.

Keywords: Friedel-Craft acetylation, 8-Hydroxyquinoline, Chalcones.

INTRODUCTION

By replacing the methyne group of naphthalene with iso-electronic species nitrogen atom forms the heterocycle quinoline. Quinoline and its derivatives have been exhibiting broad opening to pharmacological activities. The halogenated derivatives of 8-hydroxy quinolines are the good chelator for copper, zinc and iron metal ions and these halogenated compounds exhibits immense biological activity. These compounds are the promising scaffolds against many non-communal diseases such as cancer, Alzheimer's and Parkinson's disease [1-3]. In recent years, aluminium complexes of 8-hydroxyquinoline derivatives exhibit organic light emitting diode (OLEDs) property, used in electroluminescent devices [4]. Introduction of nitro group to organic molecule generally requires harsh condition such as nitrating mixture (conc. sulphuric and nitric acid) but in case of quinolines amines can be nitrated easily at C-5 or C-7 position by using sodium nitrite and copper nitrate as catalyst cheap catalyst with excellent yield. The reaction proceeds *via* C-H activation process [5].

8-Hydroxyquinoline shows good chelation with wide range of metal ions includes *s*-, *p*-, *d*- and *f*-block elements. The main trend and selectivity is forming stable, insoluble complex with metal ion with any one oxidation state. While the same metal ion with other oxidation state is not favorable leads the quinoline molecule redox reaction. It forms strong complex with ferric ions while ferrous ions are oxidized to ferric ions [6]. The derivatives of 8-hydroxy quinoline are good inhibitors enzyme Ras protease. These enzymes are present in endoplasmic reticulum which is responsible of caaX proteins, there by plays significant role in cell signaling process. Quionolines which forms square planar complexes with first row transition elements and these complexes tend to show DNA binding property and anticancer activity [7]. 8-Hydroxyquinoline bidentate ligand but coordination number varies according to the nature of metal ions. Aluminum ion forms octahedral, zinc and magnesium ions forms distorted tetrahedral,cadmium and zinc ions forms bimetallic complexes [8]. The Ru^{II} (η_6-*p*-cymene) complexes exhibit the minor impact on cytotoxicity [9]. The impressing biological significance of quinoline scaffolds makes us for the synthesis of acetyl derivatives. Herein, we reported the synthesis of 5-acetyl-8-hydroxy quinoline by one pot synthesis. The phenolic and acetyl group in the 8th and 5th position can be post transformed to other active groups.

Further chalcones are the important scaffolds which is represented by α,β-unsaturated ketone group which is sandwitched between any two aromatic groups. Chalcones are naturally occurring in many floras and are of great medicinal importance. The flora families Leguminaceae, Fabaceae, zinzeberaceae, Fabaceae contains chalcones and are used in folk medicines. Numerous literatures revealed the importance of these chalcone scaffolds [10]. In this perspective, we planned to construct chalcones containing 8-hydroxy quinoline moiety. Chalcones are chief precursor for variety of heterocyclic compounds with heteroatoms nitrogen, sulphur, oxygen, *etc*. [11,12], The size of heterocyclic ring may vary from three membered ring such as aziridnes [13] to seven-membered rings such as benzothiazepines [14]. Five-membered rings such as pyrazolins, pyrazoles, pyrazole carboxamide and pyrazole thiamides [15-20].

EXPERIMENTAL

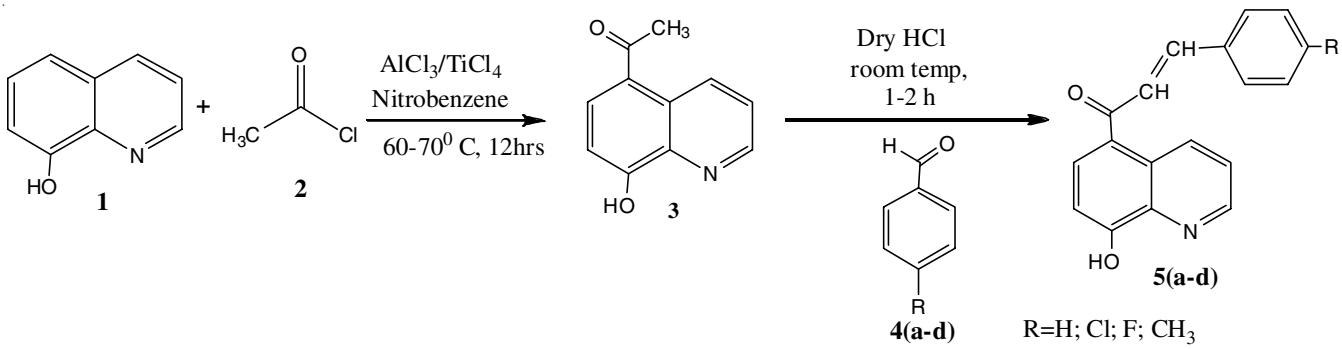
Melting points were determined by an open capillary tube method and are uncorrected. Purity of the compounds was checked on thin layer chromatography plates precoated with silica gel using the solvent system ethyl acetate: *n*-hexane (1:4 v/v). The spots were visualized under UV light and also using iodine chamber. ^{1}H NMR were recorded using 400 MHz Agilent-NMR spectrometer. The solvent $CDCl_3$ with TMS as an internal standard was used to record the spectra. The chemical shifts are expressed in δ ppm. Mass spectra were obtained on ESI/ APCI-Hybrid Quadrupole, Synapt G2 HDMS ACQUITY UPLC model spectrometer. Elemental analysis was obtained on a Thermo Finnigan Flash EA 1112 CHN analyzer. Purification of compounds was done by column chromatography on silica gel (70-230 mesh Merck)

X-ray diffraction studies: Single crystals of suitable dimensions were chosen carefully for X-ray diffraction studies. The X-ray intensity data of the compounds were collected using Rigaku XtaLAB Mini diffractometer with X-ray generator operating at 50 kV, 12 mA and Mo*K*α radiation. Data were collected with χ fixed at 54º, for different settings of φ (0º and 360º), keeping the scan width of 0.5º with exposure time of 4 s and the sample to detector distance was fixed to 50 mm. The complete intensity data sets were processed using CRYSTAL CLEAR [15]. The crystal structures were solved by direct method and refined by full-matrix least squares method on F^2 using SHELXS and SHELXL programs [16,17]. All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were positioned geometrically. After several cycles of refinement, the final difference Fourier map showed peaks of no chemical significance and the residuals were saturated to accepted values. The geometrical calculations were carried out using the program PLATON [18]. The molecular and packing diagrams were generated using the software MERCURY [19].

Synthesis of 5-acetyl-8-hydroxyquinoline (3): To a solution of acetyl chloride (**2**) (1.62 g, 20 mmol) in nitrobenzene (3-5 mL), introduce 8-hydroxyquinoline (**1**) (3 g, 20 mmol), a yellow folculant precipitate out. To a above reaction mixture, added about 5 g aluminium chloride/titanium chloride with constant shaking, the precipitate disappeared and a clear semi-solid was resulted. It was kept at 70 ºC for 12 h in a flask fitted with a calcium chloride tube. On cooling, some crushed ice and 100 mL 10% HCl was added to it and the separated nitrobenzene was driven off with steam. On standing overnight, the separated hydrochloride of 5-acetyl-8-hydroxyquinoline (**3**) was filtered. It was dissolved in water and on the addition of sodium acetate to it, the free base separated out. It was recrystallized from hot water; (55% of the theoretical) after recrystallization. Compound **3** is colourless hair-like needles from hot water (**Scheme-I**). Yield 55%; m.p.: 112-114 ºC; MS *m/z*: 187.06 (100.0%) (M+); Anal. calcd. (found) for $C_{11}H_9NO_2$ (%): C, 70.58 (70.51); H, 4.85 (4.78); N, 7.48 (7.43).

Synthesis of 1-(8-hydroxyquinolin-5-yl)-3-(arylidene)-prop-2-en-1-one (5a-d): To a solution mixture of 5-acetyl-8-hydroxyquinoline (**3**, 10 mmol) and aromatic aldehydes (**4a-d**, 10 mmol) in ethyl alcohol, dry HCl was passed through the bend tube for about 3-5 min. The solution mixture was stirred at room temperature for 1-2 h. The progress of the reaction was monitored by TLC. After the completion, the precipitation of the reaction mixture was occurred indicating the completion of the reaction. The solids separated were filtered, washed successively with 2% aqueous sodium carbonate. The crude solids were recrystallized from ethanol to obtain 1-(8-hydroxyquinolin-5-yl)-3-(aryl)prop-2-en-1-one (**5a-d**) in moderate yield (**Scheme-I**).

1-(8-Hydroxyquinolin-5-yl)-3-phenylprop-2-en-1-one (5a): Yield 67%, m.p.: 233-235 ºC; ^{1}H NMR: δ 7.06 (d, 1H, COCH), 6.68 (s, 1H, Ar-H), 7.43 (d, 2H, Ar-H) 7.38 (d, 2H, Ar-H), 7.51 (m, 1H, Ar-H), 7.54 (d, 2H, Ar-H), 8.06 (d, 1H, =CH), 8.42-8.97 (m, 3H, Ar-H), 9.02 (s, 1H, -OH); MS *m/z*: 275.09 (100.0%) (M+); Anal. calcd. (found) for $C_{18}H_{13}NO_2$ (%): C, 78.53 (78.50); H, 4.76 (4.70); N, 5.09 (5.03).



Scheme-I: Reaction pathway for the synthesis of 1-(8-hydroxyquinolin-5-yl)-3-(aryl)prop-2-en-1-one **5(a-d)**

3-(4-Chlorophenyl)-1-(8-hydroxyquinolin-5-yl)prop-2-en-1-one (5b): Yield 72%, m.p. 276-278 ºC; ^{1}H NMR: δ 6.58 (d, 1H, COCH), 7.16 (d, 2H, Ar-H), 7.29 (m, 2H, Ar-H), 7.75 (d, 1H, =CH), 7.87 (d, 2H, Ar-H), 8.48-8.6 (m, 3H, Ar-H), 9.01 (s, 1H, -OH); MS *m/z*: 309.05 (100.0%) (M+), 311.05 (32.0%) (M+2); Anal. calcd. (found) for $C_{18}H_{12}NO_2Cl$ (%): C, 69.80 (69.76); H, 3.91 (3.86); N, 4.52 (4.48).

3-(4-Fluorophenyl)-1-(8-hydroxyquinolin-5-yl)prop-2-en-1-one (5c): Yield 70%, m.p.: 246-248 ºC; ^{1}H NMR: δ 6.72 (d, 1H, COCH), 7.43 (d, 2H, Ar-H), 7.41 (m, 2H, Ar-H), 7.81 (d, 1H, Ar-H), 7.93 (d, 2H, =CH), 8.652-8.73 (m, 3H, Ar-H), 8.97 (s, 1H, -OH); MS *m/z*: 293.08 (100.0%), (M+); Anal. calcd. (found) for $C_{18}H_{12}NO_2F$ (%): C, 73.71 (73.69); H, 4.12 (4.10); N, 4.78 (4.72).

1-(8-Hydroxyquinolin-5-yl)-3-(*p*-tolyl)prop-2-en-1-one, (5d): Yield 70%, m.p.: 257-259 ºC; ^{1}H NMR: δ 2.39 (s, 3H, CH_3), 6.64 (d, 1H, COCH), 7.26 (d, 2H, Ar-H), 7.34 (m, 2H, Ar-H), 7.79 (d, 1H, Ar-H), 7.93 (d, 2H, =CH), 8.432-8.532 (m, 3H, Ar-H), 8.93 (s, 1H, -OH); MS *m/z*: 289.11 (100.0%) (M+); Anal. calcd. (found) for $C_{19}H_{15}NO_2$ (%): C, 78.87 (78.81); H, 5.23 (5.20); N, 4.84 (4.78).

RESULTS AND DISCUSSION

The synthetic procedure involves a solution of 8-hydroxyquinoline containing nitrobenzene acetyl chloride was introduced which causes the formation of yellow precipitate. To a reaction mixture, 1 equivalent of anhydrous $AlCl_3$ or $TiCl_4$ was added and fitted with a guard tube and reaction mixture was heated to 60-70 ºC for 12 h. After the completion of reaction mixture, 6M HCl was added and driven off the nitrobenzene by steam distillation. The aqueous layer was kept overnight and yellow crystals of hydrochloride salt were formed. The crystals were collected and on addition of aqueous sodium acetate leads to the formation of 5-acetyl-8-hydroxyquinoline (**3**) in average yield.

The effect of temperature plays an important role in Fries rearrangement at low temperature 60-70 ºC, where the acetyl group is migrated to *para*-position to the phenolic group, but at high temperature above 120 ºC mainly favours the formation of *ortho*-isomer and at ambient temperature it gives both *ortho*- and *para*-isomers. Herein, the *para*-position is favoured by maintaining the low temperature. After the confirmation of the acetylated product, then it was condensed with various aromatic aldehydes. Normal Claisen-Schmidth condensation reaction under basic condition such as NaOH/KOH often leads to poor yield, so it was planned to synthesize under acidic condition. The dry HCl was passed on to the reaction mixture. To a solution of 5-acetyl-8-hydroxyquinoline (**3**) in ethanol, aromatic aldehydes were added with constant stirring. After 5 min, catalytic amount of dry HCl was passed on to the reaction mixture using a passing tube. The resultant mixture was stirred for 1-3 h. The completion of the reaction was monitored by the TLC plates. After the completion of reaction, the mixture was poured into ice-cold water. The precipitate formed was filtered and washed with 2% aqueous sodium carbonate solution. The product was dried and purified by recrystallization using ethanol as solvent.

The compound **3** (CCDC: 1922218) crystallized as pale yellow coloured needle shaped crystals suitable for single crystal X-ray diffraction (crystal size 0.24 mm × 0.24 mm × 0.24 mm). The crystal structure was found to be monoclinic, $P2_1/c$. The Oak Ridge Thermal-Ellipsoid Plot Program (ORTEP) diagram of molecule **3** with thermal ellipsoids drawn at 50% probability and packing of molecules are shown in Figs. 1 and 2 respectively.

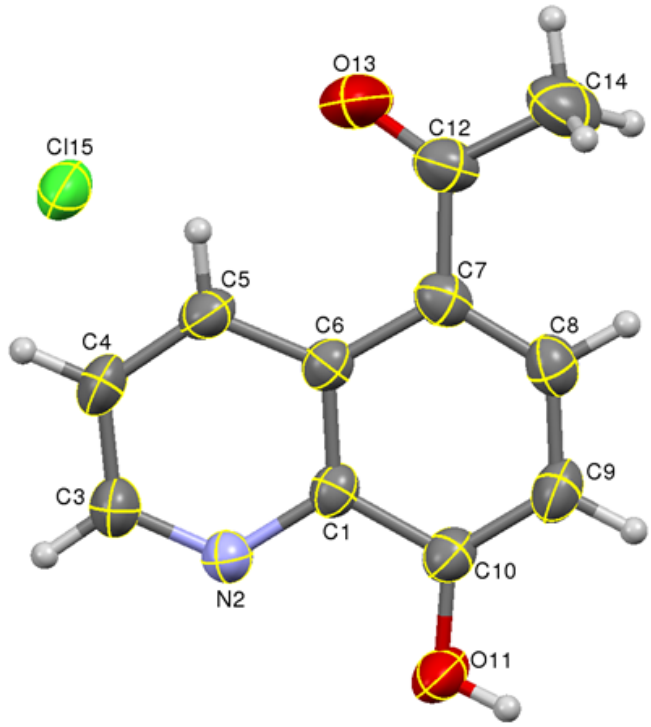


Fig. 1. ORTEP of the molecule 5-acetyl-8-hydroxyquinoline (**3**) drawn at 50% probability level

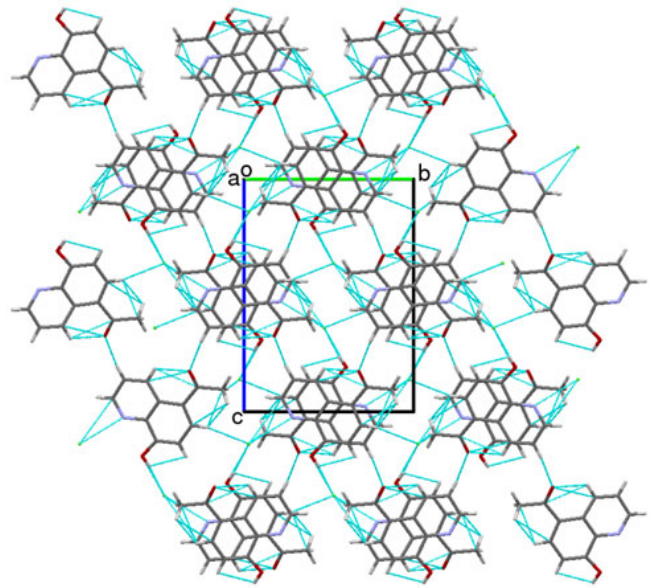


Fig. 2. Packing of molecules when viewed down along a axis

Further the chalcones formed were also characterized by spectral studies. In ^{1}H NMR analysis by considering compound

5d as representative compound among the series, the alkenyl proton each for -C=CH and -CH=C appeared as doublets at δ 6.631-6.653 (*J* = 8.8 Hz) and 7.780-7.818 (*J* = 15.2 Hz) ppm respectively. High range coupling constant (*J* = 8.8-15.2 Hz) confirms *E*-geometry around olefinic bond. The signals appeared as singlet for three protons at δ 2.39 were assigned to CH_3 protons attached to phenyl ring. In the aromatic region due to methyl substitution at *para*-position, the two doublets are appeared in the region of 7.251-7.271 and 7.920-7.940 ppm, respectively for four aromatic protons. A group of multiplets are observed in the aromatic region 7.322-7.361 and 8.432-8.532 ppm attributed to aromatic protons. The highly deshielded phenolic group attached appears as singlet at 8.932 ppm. further, the mass spectrum provides the molecular ion peak at *m/z* 289.11 confirms the formation of 1-(8-hydroxyquinolin-5-yl)-3-(*p*-tolyl)prop-2-en-1-one (**5d**). Similar and consistent pattern signals were observed in ^{1}H NMR, mass spectra and elemental analysis of the synthesized compounds **5(a-d)**, which strongly evidences the structure for the synthesized compounds.

Data value and validation: Compound 1-(8-hydroxyquinolin-5-yl)ethan-1-one (**3**) crystallizes in the monoclinic $P2_1/c$ space group with unit cell parameters *a* = 7.439(13) Å , *b* = 10.033(16) Å, *c* = 13.767(2) Å, α = 90º, β = 93.306(7)º and *Z* = 4. The molecular structure assumes the acetyl group attached to the fifth position to the quinoline ring as expected. The migration of acetyl group can be achieved by temperature at lower temperature 60-70 ºC to the fifth position, higher temperature leads to seventh position. The ORTEP of a molecule with displacement ellipsoids drawn at 50% probability level is shown in Fig. 1. The molecules exhibit layered stacking when viewed down along the *a*-axis as shown in Fig. 2. Crystal data, and structure refinement data, bond lengths, bond angles and torsion angles are given in Tables 1-4.

The title compound is confirmed as the molecular ion. The free Cl^- ion is also crystallized with the title compound. The molecular structure is stabilized with the hydrogen bond interactions of the type C-H...O and O-H...Cl. The hydrogen bond geometry is given in Table-5. The structure is also stabilized by π···π interaction [20-22]. The *Cg*(1)···*Cg*(2) (*Cg*(1) is the centroid of the ring N(2)-C(1)-C(6)-C(5)-C(4)-C(3) and *Cg*(2) is the centroid of the ring C(1)-C(6)-C(7)-C(8)-C(9)-C(10) with a *Cg*-*Cg* distance of 3.605(6) Å, α = 2.83(12)º, β = 18.5º, γ = 21.2º, a perpendicular distance of *Cg*(2) on *Cg*(1) is -3.3609 (10) Å and a symmetry code of *-x, 1-y, -z*.

Conclusion

An easily accessible and convenient Friedel-Craft procedure for the synthesis of acetylation of quinoline rings were revealed in this study. Further the post transformation of acetyl group to chalcones is also represents the worth of this work. The structure of chloride salt of 5-acetyl-8-hydroxyquinoline is studied by single crystal X-ray diffraction studies. The compound crystallizes in the monoclinic crystal system with the space group $P2_1/c$. The molecular structure is stabilized with the hydrogen bond interactions of the type C-H...O, O-H...Cl and π···π interactions.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT DETAILS OF THE COMPOUND 5-ACETYL-8-HYDROXYQUINOLINE (**3**)

Empirical formula	$C_{11}H_9NO_2Cl$
CCDC	1922218
Formula weight	222.64
Temperature	293 K
Wavelength	0.71073 Å
Reflections for cell determination	3808
Crystal system	Monoclinic
Space group	P21/c
Cell dimensions	a = 7.439(13) Å; b = 10.033(16) Å; c = 13.767(2) Å α = γ = 90° and β = 93.306(7)°
Volume	1026(2) Å^3
Z	4
Density (calculated)	1.441 Mg m^{-3}
Absorption coefficient	0.349 mm^{-1}
F_{000}	460
Crystal size	0.240 × 0.240 × 0.240 mm
θ range for data collection	3.41° to 27.50°
Index ranges	-9 ≤ h ≤ 9; -12 ≤ k ≤ 12; -17 ≤ l ≤ 5
Reflections collected	3808
Independent reflections	2297 [Rint = 0.0497]
Refinement method	Full matrix least-squares on F^2
Data/restraints/parameters	2297 / 0 / 138
Goodness-of-fit on F^2	1.059
Final [I > 2σ(I)]	R_1 = 0.0577, wR_2 = 0.1493
R indices (all data)	R_1 = 0.0774, wR_2 = 0.1692
Extinction coefficient	CIF-file generated for 8HQAC $P2_1/c$ R = 0.06
Largest diff. peak and hole	0.669 and -0.352 e Å^{-3}

TABLE-2
BOND LENGTHS (Å)

Atoms	Bond length	Atoms	Bond length
O11-C10	1.339(4)	C5-C6	1.413(4)
O13-C12	1.211(5)	C6-C7	1.443(4)
N2-C3	1.323(4)	C7-C8	1.371(4)
N2-C1	1.375(4)	C7-C12	1.487(5)
C1-C6	1.406(4)	C8-C9	1.399(5)
C1-C10	1.421(4)	C9-C10	1.366(5)
C3-C4	1.377(5)	C12-C14	1.502(5)
C4-C5	1380(5)	–	–

TABLE-3
BOND ANGLES (°)

Atoms	Angle	Atoms	Angle
C1-N2-C3	122.2(2)	C8-C7-C12	120.4(2)
N2-C1-C6	120.1(2)	C6-C7-C12	121.8(2)
N2-C1-C10	117.4(2)	C7-C8-C9	123.7(3)
C6-C1-C10	122.5(2)	C8-C9-C10	120.0(2)
N2-C3-C4	120.6(3)	O11-C10-C9	126.5(2)
C3-C4-C5	119.4(3)	C1-C10-C9	118.2(2)
C4-C5-C6	121.1(2)	O11-C10-C1	115.3(2)
C1-C6-C7	117.8(2)	O13-C12-C14	119.2(3)
C5-C6-C7	125.6(2)	C7-C12-C14	119.6(3)
C1-C6-C5	116.6(2)	O13-C12-C7	121.2(3)
C6-C7-C8	117.8(2)	–	–

TABLE-4
TORSION ANGLES (°)

Atoms	Angle	Atoms	Angle
C3-N2-C1-C6	-2.3(4)	C4-C5-C6-C7	-178.0(2)
C3-N2-C1-C10	176.4 (2)	C1-C6-C7-C8	-1.6(3)
C1-N2-C3-C4	1.0(4)	C1-C6-C7-C12	176.8(2)
N2-C1-C6-C5	1.9(3)	C5-C6-C7-C8	176.1(2)
N2-C1-C6-C7	179.8(2)	C5-C6-C7-C12	-5.5(4)
C10-C1-C6-C5	-176.8(2)	C6-C7-C8-C9	1.2(4)
C10-C1-C6-C7	1.1(3)	C12-C7-C8-C9	-177.3(2)
N2-C1-C10-O11	-0.5(3)	C6-C7-C12-O13	-15.6(4)
N2-C1-C10-C9	-178.8(2)	C6-C7-C12-C14	167.2(3)
C6-C1-C10-O11	178.2(2)	C8-C7-C12-O13	162.8(3)
C6-C1-C10-C9	-0.1(4)	C8-C7-C12-C14	-14.4(4)
N2-C3-C4-C5	0.6(4)	C7-C8-C9-C10	-0.1(4)
C3-C4-C5-C6	-0:9(4)	C8-C9-C10-O11	-178.5(2)
C4-C5-C6-C1	-0.3(3)	C8-C9-C10-C1	-0.4(4)

TABLE-5
GEOMETRIC PARAMETERS FOR
HYDROGEN BOND INTERACTIONS (Å, °)

D–H···A	D–H	H···A	D···A	D–H···A
C(5)---H(5)...O(13)*	0.93	2.21	2.818(6)	122
C(4)---H(4)...O(13)i	0.93	2.39	3.242(7)	152
O(11)---H(11)...Cl(15)ii	0.82	2.12	2.936(6)	172

*Intra, inter- i: 1-*x*, 1/2+*y*, 1/2-*z*; ii: -*x*, 1-*y*, -*z*.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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