(E)-6,6′-(Diazene-1,2-diyl)bis(1,10-phenanthrolin-5-ol) trichloromethane disolvate: a superconjugated ligand

Muhib Ahmed  
*National University of Ireland, Maynooth*

Michael Devereux  
*Technological University Dublin, Michael.Devereux@tudublin.ie*

Vickie McKee  
*University of Southern Denmark*

Malachy McCann  
*National University of Ireland, Maynooth*

A. Denise Rooney  
*National University of Ireland, Maynooth*

Follow this and additional works at: [https://arrow.tudublin.ie/materart](https://arrow.tudublin.ie/materart)

Part of the Chemistry Commons

**Recommended Citation**

Ahmed, M., Devereux, M., McKee, V., McCann, M. & Rooney, A. D. (2019). E)-6,6′-(Diazene-1,2-diyl)bis-(1,10-phenanthrolin-5-ol) trichloromethane disolvate: a superconjugated ligand. *Crystallographic Communications, 75*(8), pp.1224-1227. doi:10.1107/S205698901900954X

This Article is brought to you for free and open access by the Materials Synthesis and Applications at ARROW@TU Dublin. It has been accepted for inclusion in Articles by an authorized administrator of ARROW@TU Dublin. For more information, please contact yvonne.desmond@tudublin.ie, arrow.admin@tudublin.ie, brian.widdis@tudublin.ie.

This work is licensed under a [Creative Commons Attribution-Noncommercial-Share Alike 3.0 License](https://creativecommons.org/licenses/by-nc-sa/3.0/).
Phenanthroline ligands are important metal-binding molecules which have been extensively researched for applications in both material science and medicinal chemistry. Azobenzene and its derivatives have received significant attention because of their ability to be reversibly switched between the $E$ and $Z$ forms and so could have applications in optical memory and logic devices or as molecular machines. Herein we report the formation and crystal structure of a highly unusual novel diazo-diphenanthroline compound, $\text{C}_{24}\text{H}_{14}\text{N}_{6}\text{O}_{2}/\text{C}_{1}\text{Cl}_{2}\text{CHCl}_{3}$.  

1. Chemical context

The chemical versatility of 1,10-phenanthroline (phen), its substituted derivatives and corresponding metal complexes (Bencini & Lippolis, 2010) is exemplified by their uses as organic light-emitting diodes (OLED)/electroluminescent display and solid-state lighting materials (Li et al., 2009), fluorescence molecular probes and imaging agents (Haraga et al., 2018), ion sensors (Zheng et al., 2012), solar energy converters (Freitag et al., 2016), anti-cancer and antimicrobial cytotoxins (McCann et al., 2012), DNA/RNA binding/cleavage (Kellett et al., 2011), enzyme inhibitors (Zhu et al., 2015), biomimetics (Casey et al., 1994) and catalysts (Lu et al., 2015). Given the resourcefulness of phenanthrolines, there is a continuing demand for new molecules containing this structural motif.

Herein, we detail the preparation and structural characterization of the purple diazo-diphenanthroline compound, $(E)-6,6'-(\text{diazene}-1,2-diyl)bis(1,10\text{-phenanthrolin}-5\text{-ol})$ (I), which was isolated in low yield from the reaction between 1,10-phenanthroline-5,6-dione (phendione) and isonicotinic acid hydrazide (isoniazid). Compound I crystallizes with two trichloromethane solvate molecules ($1/\text{C}_{1}\text{Cl}_{2}\text{CHCl}_{3}$). The fully conjugated bis-phenanthroline molecule I is expected to offer exciting new physical and chemical properties as a stand-alone...
organic molecule, and it will also birth a plethora of interesting metal coordination complexes as a consequence of the dual $N,N'$-1,10-phenanthroline chelating moieties situated on the opposite ends of the molecule.

2. Structural commentary

Compound 1·2CHCl₃ crystallizes with two molecules of trichloromethane solvate per diazo-diphenanthroline (Fig. 1). The molecule lies on a centre of symmetry and is essentially planar, the r.m.s. deviation from the plane of the atoms in the ring system is 0.259 Å. The molecules lie parallel to the (5 7 15) or (5 7 14) planes. There is a hydrogen bond between the alcohol and the diazo linker [O1—H1A···N2' = 0.88 (3) Å under symmetry operation $-x + 2, -y + 1, -z + 1$, Table 1] and the trichloromethane molecule is oriented by a bifurcated C—H···N interaction with the phenanthroline moiety [3.219 (3) and 3.136 (4) Å to N1 and N3, respectively]. The carbon atom of the trichloromethane molecule (C21) is 1.045 (3) Å from the mean plane of 1·2CHCl₃. There are 40 examples in the Cambridge Structural Database (CSD, Version 5.40, update of May 2019; Groom et al., 2016) showing similar interactions between trichloromethane and 1,10-phenanthroline derivatives and the geometry for 1·2CHCl₃ is typical of the group [mean Cl₃CH···N = 3.18 (5) Å].

The bond lengths indicate some delocalization through the central part of the molecule. The C6—O1 and C5—N2 bonds are short [1.318 (3) and 1.376 (3) Å, respectively] and the N=N bond, at 1.316 (4) Å, is significantly longer than in most free diazo molecules [mean of 1.24 (4) Å for 2730 CSD entries].

3. Supramolecular features

Fig. 2 shows the unit-cell packing, the molecules lie parallel to the (5 7 15) or (5 7 14) planes with a mean interplanar distance of 3.228 (2) Å (under $-x + 2, -y + 1, -z + 1$) and the axis of the stack runs parallel to the $a$ axis. The shortest ring centroid–centroid distance is 3.5154 (15) Å between the C₆ rings; however, there is a more direct overlap between the diazo group and an imine group in the next layer (ca 3.246 Å between the mid-point of the N=N bond and the mid-point of the C11=N3 bond under symmetry operation $1 - x, 1 - y, 1 - z$) (Fig. 3). The most notable interactions between stacks are type $R$—Cl···$R$ packing interactions (Mukherjee et al., 2014; Cavallo et al., 2016), the shortest Cl···Cl distance being 3.5353 (11) Å for Cl1···Cl3 under symmetry operation $-1 + x, y, z$.

4. Database survey

There are three published examples of molecules containing the 2,2′-dihydroxyazoazobenzene core (Bougueria et al., 2014; Evangelio et al., 2008; Schilde et al., 1994) and all of these are significantly less delocalized than 1·2CHCl₃.

5. Spectroscopy studies of 1 in solution

Compound 1 has a very low solubility in all organic solvents investigated (CH₃Cl, CH₂Cl₂, DMSO, CH₃CN and alcohols).
UV/vis spectra of 1,2CHCl₃ recorded in ethanol, methanol, CHCl₃ and CH₂Cl₂ are given in Fig. 4. Compound 1 exhibits significant solvatochromism showing a broad band in CHCl₃ and CH₂Cl₂ with λ_max at 543 nm. This band undergoes a bathochromic shift and separates into two bands in the alcohols with λ_max values at 643 nm and 600 nm in ethanol and at 636 nm and 591 nm in methanol. No accurate measurement of the extinction coefficient could be made as 1 was not fully soluble in the solvents and precipitation from the solvent occurred upon standing. The solubility of 1 was so low that only a very poorly resolved ¹H NMR of the compound was obtained in d₅-methanol showing a series of peaks in the region expected for the phenanthroline H-atom signals and no definitive assignments of the peaks could be made. Interestingly, 1 was more soluble in strongly acidic solutions due to the protonation of one or more of the N atoms. Compound 1 dissolved in CF₃COOD to form a bright-red solution. Six signals are observed in the ¹H NMR spectrum in the region associated with the phenanthroline peaks. This finding is consistent with a compound which has a centre of symmetry, as found for the crystal structure, and suggests that at room temperature 1 remains in the E form in this solvent.

6. Synthesis and crystallization

The mechanism to form 1 from the reaction mixture is unclear; however, the formation of isonicotinic acid N’-(pyridine-4-carbonyl)-hydrazide (2) from the mixture is an indication that radical chemistry is occurring. Isoniazid is well known to react to form radical species and these radicals are important in its role as an anti-tuberculosis drug (Timmins et al. 2006). Significantly one LC–MS study has shown that isoniazid will photo-degrade to form 2 (Fig. 5) and radical intermediates are proposed in its formation (Bhutani, 2007). Attempts were made to try to favour the formation of 1 using UV irradiation and the radical initiators azobisisobutyronitrile and 2,2’-azobisis(2-amidinopropane) dihydrochloride but these were unsuccessful. However, although the reaction to form 1 was low yielding, attempts to make 1 by reaction of 6-amino-1,10-phenanthroline-5-ol and 6-nitroso-1,10-phenanthroline-5-ol using known conditions to form diazo compounds (Zhao et al. 2011) did not form the desired product. Studies are ongoing to improve the yield of the reaction to form 1.

Phendione (0.210 g, 1.000 mmol) was added to solution of isoniazid (0.137 g, 1.000 mmol) in EtOH (25 cm³). p-Toluenesulfonic acid (10%, 0.02 g) was added and the solution refluxed for 6 h. The resulting suspension was filtered whilst hot and the filtrate allowed to stand in the dark overnight. Precipitated yellow (Z)-N’-(6-oxo-1,10-phenanthroline-5(6H)-ylidene)isonicotinohydrazide (0.263 g, 0.799 mmol, 80%) was filtered off and the bright-orange filtrate was concentrated to ca 10 cm³ using rotary evaporation and then allowed to stand in the dark. Over a period of four weeks, the bright-orange filtrate changed to a dark-green suspension. This mixture was heated to reflux and filtered whilst hot to give a green filtrate (see below) and a dark-purple powder. The powder was dissolved in CHCl₃ and allowed to crystallize over several days to produce dark-purple crystals of (E)-6,6’-(diazenie-1,2-diyldi)bis(1,10-phenanthroline-5-ol) trichloromethane disolvate (1,2CHCl₃) (0.026 g, 0.039 mmol, 62% based on isoniazid starting material). Upon leaving the above green filtrate to evaporate further white isonicotinic acid N’-(pyridine-4-carbonyl)-hydrazide (compound 2) precipitated. The supernatant was decanted off and the solid dissolved in hot acetone. This colourless solution was evaporated to dryness on a rotary evaporator to give 2 (0.015 g, 0.062 mmol, 12.4% based on isoniazid starting material).

Compound 1: IR (ATR, cm⁻¹) (1,2CHCl₃): 3065, 2108, 1583, 1568, 1500, 1472, 1415, 1338, 1284, 1227, 1162, 1027, 795, 739, 717. ¹H NMR (protonated-1) (CF₃COOD, 500 MHz): δ 9.60 (d, J = 8.5 Hz, 2H), PhenH 9.56 (d, J = 8.5 Hz, 2H, PhenH), 9.47 (d, J = 5.0 Hz, 2H, PhenH), 9.37 (d, J = 5.0 Hz, 2H, PhenH), 8.57 (dd, J = 8.5, 5.0 Hz, 2H, PhenH), 8.38 (dd, J = 8.5, 5.0 Hz, 2H, PhenH), 4.12 (s, 2H, OH). Elemental analysis calculated for C₁₄H₁₀N₆O₄ (2CHCl₃): C 75.25, H 2.45, N 12.79%; found: C 74.73, H 2.52, N 12.77%.

Compound 2 has been previously reported (Quiroga et al., 2008; Bhutani et al., 2007) and the characterization data given are consistent with the data recorded in the present study.

Compound 2: IR (KBr, cm⁻¹) 3435, 3210, 3045, 1682, 1642, 1546, 1489, 1406, 1299, 838, 751. ¹H NMR (CD₂OD, 500 MHz): δ 8.80 (d, J = 5 Hz, 2H), 8.38 (d, J = 5 Hz, 2H). ¹³C NMR (CD₂OD, 125 MHz): δ 156.6 (C=O), 150.0 (PyrC), 140.5 (PyrC), 121.8 (PyrC). MS: Calculated m/z for C₁₂H₁₄N₄O₂: (M + H)⁺ 243.0877; found: (M + H)⁺ 243.0882; difference (ppm): 2.15.
7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C-bound H atoms were included in calculated positions and treated as riding, with C—H = 0.95–1.00 Å and Uiso(H) = 1.5Ueq(C) for methyl H atoms or 1.2Ueq(C) otherwise. The H atom (H1A) bonded to oxygen was located in a difference-Fourier map and its coordinates were refined with Uiso(H) = 1.5Ueq(O).

Acknowledgements

We gratefully acknowledge Maynooth University for a John and Pat Hume Scholarship for MA.

Funding information

Funding for this research was provided by: National University of Ireland, Maynooth Hume Scholarship (scholarship to Muhib Ahmed).

References

Bencini, A. & Lippolis, V. (2010). Coord. Chem. Rev. 254, 2096–2180. Bhutani, H., Singh, S., Vir, S., Bhutani, K. K., Kumar, R., Chakraborti, A. K. & Jindal, K. C. (2007). J. Pharm. Biomed. Anal. 43, 1213–1220. Bougueria, H., Mili, A., Benosmane, A., el Kader Bouchoul, A. & Bouaoud, S. (2014). Acta Cryst. E70, o225. Bruker (2010). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA. Casey, M. T., McCann, M., Devereux, M., Curran, M., Cardin, C., Convery, M., Quillet, M. & Harding, C. (1994). J. Chem. Soc. Chem. Commun. pp. 2643–2645.

Table 2

| Crystal data | Chemical formula | C24H14N6O2-2CHCl3 |
|--------------|-----------------|--------------------|
| Crystal system, space group | Monoclinic, P21/c |
| Temperature (K) | 150 |
| a, b, c (Å) | 5.9406 (7), 18.856 (2), 12.2375 (16) |
| β (°) | 96.863 (4) |
| V (Å³) | 1361.0 (3) |
| Z | 2 |
| Radiation type | Mo Kα |
| μ (mm⁻¹) | 0.67 |
| Crystal size (mm) | 0.43 × 0.05 × 0.04 |

Data collection

Diffractometer | Bruker-Nonius X8 APEXII CCD |
Absorption correction | Multi-scan (SADABS; Sheldrick, 2012) |

Tmin, Tmax | 0.657, 0.745 |

No. of measured, independent and observed | 18529, 2732, 2068 |

Rmax (sin(θ/λ))max (Å⁻¹) | 0.620 |

Refinement

R[F² > 2σ(F²)], wR(F²), S | 0.044, 0.111, 1.03 |
No. of reflections | 2732 |
No. of parameters | 184 |
H-atom treatment | Heteroxyz |
Δρmax, Δρmin (e Å⁻³) | 0.87, −0.59 |

Computer programs: APEX2 and SAINT (Bruker, 2010). SHELXT (Sheldrick 2015a). SHELXL2018 (Sheldrick, 2015b). Mercury (Macrae et al., 2008) and publCIF (Westrip, 2010).

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodrigue-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). J. Appl. Cryst. 41, 466–470.

Mugherjee, A., Thothadi, S. & Desiraju, G. R. (2014). Acc. Chem. Res. 47, 2514–2524.

Quiriga, J., Portilla, J., Abonia, R., Insauty, B., Nogueras, M. & Cobo, J. (2008). Tetrahedron Lett. 49, 5943–5945.

Schildle, U., Hefele, H., Ludwig, E. & Uhlemann, E. (1994). Cryst. Res. Technol. 29, 393–396.

Sheldrick, G. M. (2012). SADABS. University of Göttingen, Germany.

Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.

Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.

Timmins, G. S. & Deretic, V. (2006). Mol. Microbiol. 62, 1220–1227.

Zheng, Y., Tan, C., Drummen, G. P. & Wang, Q. (2012). Spectrochim. Acta A Mol. Biomol. Spectrosc. 96, 387–394.

Zhu, Y., Liao, Y., Zhang, L. & Bai, X. (2015). PCT Int. Appl. WO 2015154716 A1.

Acta Cryst. (2019). E75, 1224–1227

Ahmed et al. • C24H14N6O2-2CHCl3

1227
supporting information

Acta Cryst. (2019). E75, 1224-1227  [https://doi.org/10.1107/S205698901900954X]

(E)-6,6′-(Diazene-1,2-diyl)bis(1,10-phenanthrolin-5-ol) trichloromethane disolvate: a superconjugated ligand

Muhib Ahmed, Michael Devereux, Vickie McKee, Malachy McCann and A. Denise Rooney

Computing details

Data collection: APEX2 (Bruker, 2010); cell refinement: SAINT (Bruker, 2010); data reduction: SAINT (Bruker, 2010); program(s) used to solve structure: SHELXT (Sheldrick 2015a); program(s) used to refine structure: SHELXL2018 (Sheldrick, 2015b); molecular graphics: Mercury (Macrae et al., 2008); software used to prepare material for publication: publCIF (Westrip, 2010).

(E)-6,6′-(Diazene-1,2-diyl)bis(1,10-phenanthrolin-5-ol) trichloromethane disolvate

Crystal data

C24H14N6O2⋅2CHCl3  

F(000) = 664  

Dx = 1.604 Mg m−3  

Mo Kα radiation, λ = 0.71073 Å  

Cell parameters from 5155 reflections  

θ = 2.7–26.1°  

µ = 0.67 mm−1  

T = 150 K  

Lath, purple  

0.43 × 0.05 × 0.04 mm

Data collection

Bruker–Nonius X8 APEXII CCD diffractometer  

18529 measured reflections  

2732 independent reflections  

2068 reflections with I > 2σ(I)  

Rint = 0.045  

θmax = 26.2°, θmin = 2.7°  

h = −5→7  

k = −23→23  

l = −15→14

Refinement

Refinement on F2  

Least-squares matrix: full  

R[F2 > 2σ(F2)] = 0.044  

wR(F2) = 0.111  

S = 1.02  

2732 reflections  

184 parameters  

0 restraints

Primary atom site location: dual  

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed  

Heteroxyz  

w = 1/[σ2(Fo2) + (0.0444P)2 + 1.8407P]  

where P = (Fo22 + 2Fc2)/3  

(Δ/σ)max = 0.001  

Δρmax = 0.87 e Å−3  

Δρmin = −0.59 e Å−3

 sup-1
Supporting information

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 (Å²)

|    | x        | y        | z        | U₁₁    | U₂₂    | U₃₃    | U₁₂    | U₁₃    | U₂₃    |
|----|----------|----------|----------|--------|--------|--------|--------|--------|--------|
| N1 | 0.3174 (4) | 0.63628 (11) | 0.66898 (18) | 0.0216 (5) |
| C1 | 0.3648 (5) | 0.69741 (14) | 0.6234 (2) | 0.0240 (6) |
| H1 | 0.269904 | 0.736919 | 0.632910 | 0.029* |
| C2 | 0.5456 (5) | 0.70706 (14) | 0.5623 (2) | 0.0255 (6) |
| H2 | 0.572645 | 0.752054 | 0.531450 | 0.031* |
| C3 | 0.6846 (4) | 0.65044 (14) | 0.5473 (2) | 0.0219 (6) |
| H3 | 0.810516 | 0.656051 | 0.507047 | 0.026* |
| C4 | 0.6383 (4) | 0.58421 (13) | 0.5923 (2) | 0.0174 (5) |
| C5 | 0.7702 (4) | 0.52078 (13) | 0.5757 (2) | 0.0177 (5) |
| N2 | 0.9396 (3) | 0.52817 (11) | 0.50912 (17) | 0.0195 (5) |
| C6 | 0.7175 (4) | 0.45623 (14) | 0.6231 (2) | 0.0195 (5) |
| O1 | 0.8303 (3) | 0.39726 (10) | 0.61010 (16) | 0.0246 (4) |
| H1A | 0.937 (6) | 0.4088 (17) | 0.569 (3) | 0.037* |
| C7 | 0.5313 (4) | 0.45226 (13) | 0.6889 (2) | 0.0191 (5) |
| C8 | 0.4726 (5) | 0.38783 (14) | 0.7366 (2) | 0.0239 (6) |
| H8 | 0.554738 | 0.345644 | 0.726050 | 0.029* |
| C9 | 0.2948 (5) | 0.38714 (15) | 0.7985 (2) | 0.0274 (6) |
| H9 | 0.251833 | 0.344474 | 0.831710 | 0.033* |
| C10 | 0.1781 (5) | 0.45015 (15) | 0.8118 (2) | 0.0253 (6) |
| H10 | 0.057433 | 0.449191 | 0.856178 | 0.030* |
| N3 | 0.2257 (4) | 0.51143 (12) | 0.76615 (18) | 0.0224 (5) |
| C11 | 0.4006 (4) | 0.51294 (13) | 0.7050 (2) | 0.0182 (5) |
| C12 | 0.4522 (4) | 0.58002 (13) | 0.6541 (2) | 0.0185 (5) |
| C21 | 0.0382 (5) | 0.64497 (15) | 0.8784 (2) | 0.0271 (6) |
| H21 | 0.087592 | 0.621547 | 0.811921 | 0.032* |
| C11 | −0.23375 (13) | 0.61485 (6) | 0.89683 (7) | 0.0493 (3) |
| C12 | 0.03861 (18) | 0.73803 (4) | 0.85952 (7) | 0.0508 (3) |
| C13 | 0.23081 (12) | 0.62261 (4) | 0.99506 (6) | 0.0333 (2) |

Atomic displacement parameters (Å²)

|    | U₁₁    | U₂₂    | U₃₃    | U₁₂    | U₁₃    | U₂₃    |
|----|--------|--------|--------|--------|--------|--------|
| N1 | 0.0234 (11) | 0.0211 (12) | 0.0208 (12) | 0.0047 (9) | 0.0050 (9) | 0.0007 (9) |
| C1 | 0.0290 (14) | 0.0208 (15) | 0.0229 (14) | 0.0070 (11) | 0.0065 (11) | 0.0003 (11) |
| C2 | 0.0330 (15) | 0.0159 (13) | 0.0279 (15) | 0.0000 (11) | 0.0054 (12) | 0.0012 (11) |
| C3 | 0.0231 (13) | 0.0216 (14) | 0.0219 (14) | −0.0011 (11) | 0.0064 (11) | −0.0016 (11) |
| C4 | 0.0192 (13) | 0.0169 (13) | 0.0160 (12) | 0.0001 (10) | 0.0008 (10) | −0.0016 (10) |
| C5 | 0.0158 (12) | 0.0196 (13) | 0.0169 (13) | 0.0011 (10) | −0.0011 (10) | −0.0021 (10) |
| N2 | 0.0180 (11) | 0.0213 (11) | 0.0193 (11) | 0.0023 (8) | 0.0020 (9) | −0.0036 (9) |
Geometric parameters (Å, °)

|                | Å   | °   |
|----------------|-----|-----|
| N1—C1          | 1.326 (3) | 0.88 (3) |
| N1—C12         | 1.355 (3) | 1.409 (4) |
| C1—C2          | 1.392 (4) | 1.409 (4) |
| C1—H1          | 0.950 | 1.371 (4) |
| C2—C3          | 1.375 (4) | 0.9500 |
| C2—H2          | 0.9500 | 1.395 (4) |
| C3—C4          | 1.405 (4) | 0.9500 |
| C3—H3          | 0.9500 | 1.328 (3) |
| C4—C12         | 1.414 (3) | 0.9500 |
| C4—C5          | 1.457 (3) | 1.352 (3) |
| C5—N2          | 1.376 (3) | 1.459 (4) |
| C5—C6          | 1.400 (4) | 1.752 (3) |
| N2—N2'         | 1.316 (4) | 1.770 (3) |
| C6—O1          | 1.318 (3) | 1.771 (3) |
| C6—C7          | 1.446 (4) | 1.0000 |

|                | Å   | °   |
|----------------|-----|-----|
| C1—N1—C12     | 117.7 (2) | 121.2 (2) |
| N1—C1—C2      | 123.8 (2) | 118.8 (2) |
| N1—C1—H1      | 118.1 | 120.6 |
| C2—C1—H1      | 118.1 | 120.6 |
| C3—C2—C1      | 118.9 (3) | 118.9 (3) |
| C3—C2—H2      | 120.5 | 120.6 |
| C1—C2—H2      | 120.5 | 120.6 |
| C2—C3—C4      | 119.3 (2) | 123.9 (2) |
| C2—C3—H3      | 120.3 | 118.0 |
| C4—C3—H3      | 120.3 | 118.0 |
| C3—C4—C12     | 117.4 (2) | 117.9 (2) |
| C3—C4—C5      | 122.8 (2) | 122.2 (2) |
| C12—C4—C5     | 119.8 (2) | 118.0 (2) |
| N2—C5—C6      | 123.3 (2) | 119.8 (2) |
| N2—C5—C4      | 116.3 (2) | 122.7 (2) |
| C6—C5—C4      | 120.4 (2) | 117.6 (2) |
### Supporting Information

| Bond                  | Distance (Å) | Angle (°) |
|----------------------|--------------|-----------|
| N2i—N2—C5           | 118.1 (3)    |           |
| O1—C6—C5            | 122.8 (2)    |           |
| O1—C6—C7            | 117.2 (2)    |           |
| C5—C6—C7            | 120.0 (2)    |           |
| C6—O1—H1A           | 106.2 (2)    |           |
| C11—C7—C8           | 118.3 (2)    |           |
| C11—C7—C6           | 120.4 (2)    |           |

Symmetry code: (i) \(-x+2, -y+1, -z+1\).

### Hydrogen-bond geometry (Å, °)

| Bond                  | Distance (Å) | H···A (Å) | D···A (Å) | D—H···A (°) |
|----------------------|--------------|-----------|-----------|-------------|
| O1—H1A···N2i         | 0.88 (3)     | 1.74 (3)  | 2.540 (3) | 149 (3)     |
| C21—H21···N1         | 1.00         | 2.36      | 3.219 (3) | 143         |
| C21—H21···N3         | 1.00         | 2.33      | 3.136 (4) | 137         |

Symmetry code: (i) \(-x+2, -y+1, -z+1\).