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ORIGINAL PAPER

PM3 semiempirical study and its comparison with X-ray crystal structure of 2-methyl-4-(4-methoxyphenylazo)phenol

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Abstract The crystal and molecular structure of 2-methyl-4-(4-methoxyphenylazo)phenol have been determined by X-ray single crystal diffraction technique. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.7763(8)$ Å, $b = 11.3966(8)$ Å, $c = 11.9531(8)$ Å and $\beta = 108.752(6)^\circ$. In addition to the molecular geometry from X-ray experiment, its optimized molecular structure has been obtained with the aid of PM3 semiempirical quantum mechanical method, and then the corresponding geometric parameters were compared with those of X-ray crystallography. To determine conformational flexibility and crystal packing effects on the molecules, molecular energy profile of the title compound was obtained with respect to two selected degrees of torsional freedom, which were varied from -180° to $+180^\circ$ in steps of 10°. Crystal structure of the title compound is a fibroid structure constructed by C–H···O and O–H···N type intermolecular hydrogen bonds. The most favorable conformer of the title compound has been determined by the crystal packing effects and there is no steric hindrance during rotation around the selected torsion angles.

Keywords Azo compound · PM3 · Crystal structure · Fibroid structure · Hydrogen bond

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Introduction

Azo compounds have been the most widely used class of dyes because of their versatile application in various fields. In particular, azo-containing photochromic organic compounds and azo-conjugated metal complexes have attracted much attention recently due to their possible applications in the area of photon-mode high-density information storage, photo-switching devices, and optical computing [1–4].

However, azobenzene is one of the representative photochromic molecules with two geometric isomers, a *trans* form and a *cis* form [5–7]. Moreover, all azo compounds may occur in one of the isomeric forms: *trans* and *cis*. The *trans*-to-*cis* isomerization occurs by photoirradiation with UV light and *cis*-to-*trans* isomerization proceeds with blue-light irradiation or by heating, because their *trans* forms are thermodynamically more stable than their *cis* forms [8, 9]. In the present paper, details of *trans* stereochemistry of the title compound by single crystal X-ray diffraction technique as part of a general study of the crystal chemistry of dyes and PM3 semiempirical quantum mechanical method to provide templates for molecular modeling studies are examined. Results obtained from both the methods were compared and crystal packing effects on the exact *trans* configuration of the title compound were comprehensively discussed.

Experimental

Synthesis of the title compound

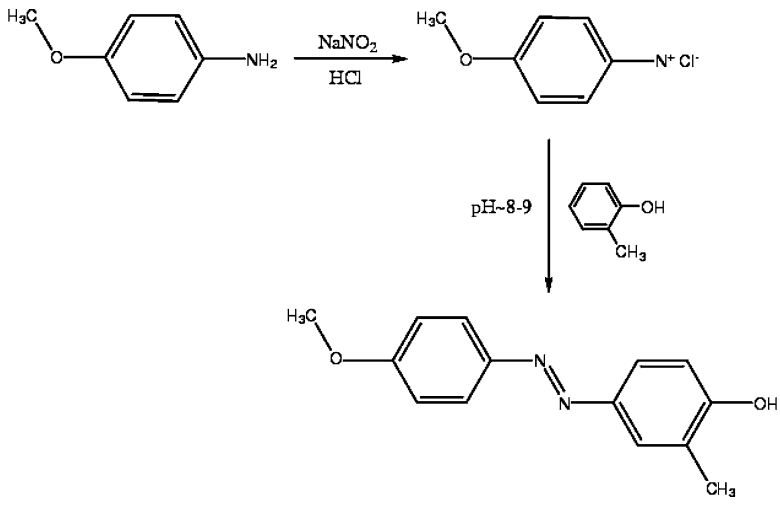
A mixture of *p*-anisidine (4 g, 32.4 mmol), water (50 ml), and concentrated hydrochloric acid (8.14 ml, 97.2 mmol) was stirred until a clear solution was obtained. This solution was cooled to 273–278 K and a solution of nitrite (3.13 g, 45.36 mmol) in water was added dropwise while the temperature was maintained below 278 K. The resulting mixture was stirred for 30 min in an ice bath. *o*-Cresol (3.5 g, 32.4 mmol) solution (pH 9) was gradually added to a cooled solution of 4-methoxybenzenediazonium chloride, prepared as described earlier, and the resulting mixture was stirred at 273–278 K for 60 min in an ice bath (see Scheme 1). The product was recrystallized from ethyl alcohol to obtain solid 2-methyl-4-(4-methoxyphenylazo)phenol. Crystals of 2-methyl-4-(4-methoxyphenylazo)phenol were obtained after 1 day by slow evaporation from acetonitrile (yield 86%, m.p. 422–424 K).

X-ray crystallography

A suitable sample of size 0.30 mm × 0.23 mm × 0.20 mm was chosen for the crystallographic study and then carefully mounted on goniometer of a STOE IPDS II diffractometer. All diffraction measurements were performed at room temperature (296 K) using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The systematic absences and intensity symmetries indicated the monoclinic $P2_1/c$ space group. A total of 16,872 reflections (2470 unique) within the θ range of ($1.79^\circ < \theta < 27.95^\circ$) were collected in the rotation mode with $R_{\text{int}} = 0.0316$. The collected intensities were corrected for Lorentz and polarization factors, for absorption correction ($\mu = 0.087$ mm^{-1}) by integration method via X-RED software [10] and cell parameters were determined by using X-AREA software [10]. Extinction correction was not applied. The structure was solved by direct methods using SHELXS-97 [11]. The refinement was carried out by full-matrix least-squares method on the positional and anisotropic temperature parameters of the non-hydrogen atoms, or equivalently corresponding to 207 crystallographic parameters. All H atoms were located in a difference Fourier map and refined independently with isotropic displacement parameters. The final C–H distances ranged from 0.92(2) to 1.01(2) Å. The structure was refined to $R_1 = 0.047$ for observed 1793 reflections, which satisfied the condition $I > 2\sigma(I)$, and to $R_1 = 0.063$ for all 2470 data used in the refinement process. The maximum peaks and the deepest hole observed in the final $\Delta\rho$ map were 0.28 and -0.16 e Å^{-3}, respectively. The scattering factors were taken from SHELXL-97 [12]. Other details of the data collection conditions and parameters of refinement process are summarized in Table 1.

Computational procedure

The *trans* symmetry imposed geometry optimization of the title molecule leading to energy minima *in vacuo* was performed by using PM3 self-consistent field molecular orbital [13, 14] method at the restricted Hartree–Fock (RHF) level [15] with the aid of WinMopac 7.21 package [16]. Non-Linear Least Squares (NLLSQ) gradient minimization routine was used in the optimization procedure with very precise GNorm of 0.01. The crystallographic coordinates were used as starting geometry for the calculations. The structure associated with the lowest energy according to the PM3 optimization was compared with the X-ray structure. To elucidate conformational features of the title molecule and crystal packing effects on the molecules, two selected degrees of torsional freedom, T(N1–N2–C8–C13) and T(N2–N1–C6–C5), were varied from -180° to $+180^\circ$ in steps of 10°, and the molecular energy profiles were obtained by performing single-point calculations on the calculated potential energy surface. In addition, heat of formation values of the two different dimeric



Scheme 1 Synthesis scheme of the title compound

Table 1 Crystallographic data for the title compound

Color/shape	Yellow/prismatic
Chemical formula	$C_{14}H_{14}N_2O_2$
Formula weight	242.27
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell parameters	
a (Å)	9.7763(8)
b (Å)	11.3966(8)
c (Å)	11.9531(8)
β (°)	108.752(6)
Volume (Å^3)	1261.08(17)
Z	4
Calculated density (g/cm^3)	1.276
Absorption coefficient (mm^{-1})	0.087
$F_{0\,0\,0}$	512.0
Diffractometer/measurement method	STOE IPDS II/rotation
h_{min}, h_{max}	−12, 12
k_{min}, k_{max}	−14, 14
l_{min}, l_{max}	−15, 15
Unique reflections measured	2470
Independent/observed reflections	2470/1793
Data/restraints/parameters	2470/0/207
Goodness of fit on F^2	1.154
R indices ($I > 2\sigma(I)$)	$R_1 = 0.0468$, $wR_2 = 0.1359$
R indices (all data)	$R_1 = 0.0631$, $wR_2 = 0.1434$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0764P)^2 + 0.07P]$; $P = (F_o^2 + 2F_c^2)/3$

structures formed by O–H···N and C–H···O type intermolecular hydrogen bonds were calculated by using single-point calculations with respect to the crystallographic coordinates so that the formation energy of these hydrogen bonds were compared and their contributions to the stability of the crystal structure were discussed.

Results and discussion

Structure determination

The title complex, an Ortep [17] view of which is shown in Fig. 1, crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The asymmetric unit in the crystal structure contains only one molecule. Non-hydrogen atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2.

In the title compound, the aromatic rings, which adopt a distorted *trans* configuration about the N=N double bond, are not coplanar with a dihedral angle of 16.01(9)° between them. In the azo groups, C8–N2 and C6–N1 bond lengths, which reflect their single bond character, are 1.428(2) and 1.432(2) Å, respectively; whereas N1–N2 bond length is 1.247(2) Å. This value obviously indicates its double bond character. Corresponding values of these bond lengths mentioned earlier for similar compounds are consistent with previously reported studies in the literature [18–25]. Although there is no intramolecular hydrogen bond, two important intermolecular hydrogen bonds, details of which are given in Table 3, are observed in the crystal structure. The geometrical parameters of the intermolecular hydrogen bonds in the crystal structure are comparable with those of similar azo compounds [18–25]. The corresponding values of the distances between donor and acceptor in C–H···O and O–H···N type hydrogen bonds were found to be 3.464(4) and 2.902(2) Åin [20, 24], respectively. In addition, the respective values of the angles of D–H···A in these hydrogen bonds are 137° and 159°. Both intermolecular hydrogen bonds in the crystal structure have electrostatic nature due to its D–H≪H···A; furthermore, according to Jeffrey's classification [26], O–H···N and C–H···O type intermolecular hydrogen bonds are regarded as moderately strong and relatively weak H-bonds, respectively.

In the crystal structure of the title compound, infinite one-dimensional parallel linear chains are constructed by linking the molecules as building blocks via C–H···O type intermolecular hydrogen bond. When these linear chains are connected with O–H···N type intermolecular hydrogen bonds, a crossed cage-wise crystal structure is obtained. Atom O1 contributes to cage architecture of the crystal structure as both donor and acceptor in two different intermolecular hydrogen bonds. The existence of cage-wise crystal structures is not a feature prevalently observed in solid state for many azo compounds, because substituted groups' oxygen atoms

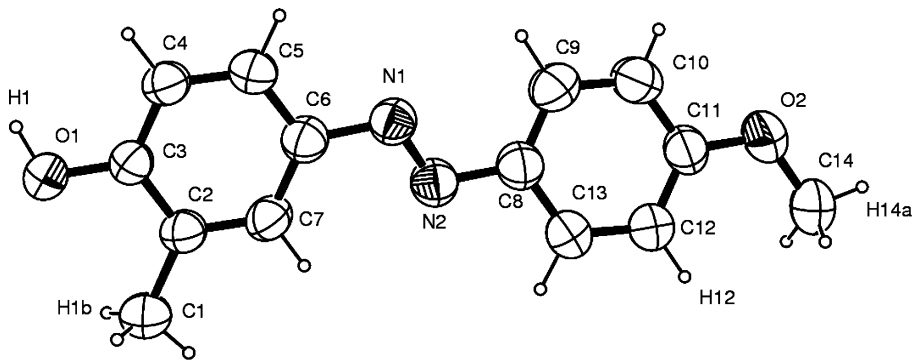


Fig. 1 Ortep drawing of the molecule indicating atom numbering scheme including hydrogen atoms that participate in forming intermolecular hydrogen bonds and edge-to-face interactions with 50% probability level

Table 2 Atomic coordinates and equivalent isotropic displacement parameters (Å^2) of the non-hydrogen atoms for the title compound

Atom	x	y	z	U_{eq}
O1	0.71133(14)	−0.01961(10)	0.37450(11)	0.0662(4)
O2	−0.05827(16)	0.74783(13)	0.43579(12)	0.0885(5)
N1	0.33966(15)	0.35582(11)	0.34716(12)	0.0583(4)
N2	0.33259(16)	0.39212(12)	0.44356(13)	0.0623(4)
C1	0.7130(3)	0.0741(2)	0.58987(17)	0.0780(8)
C2	0.61789(19)	0.12188(13)	0.47367(13)	0.0562(5)
C3	0.62131(17)	0.07286(13)	0.36700(13)	0.0526(5)
C4	0.53608(19)	0.11822(14)	0.25942(15)	0.0580(5)
C5	0.44422(19)	0.21037(15)	0.25573(15)	0.0595(6)
C6	0.43768(18)	0.25958(14)	0.35954(14)	0.0583(4)
C7	0.52563(19)	0.21476(14)	0.46766(15)	0.0589(6)
C8	0.2304(2)	0.48414(15)	0.43412(15)	0.0623(4)
C9	0.1144(2)	0.51013(18)	0.33360(17)	0.0718(7)
C10	0.0199(2)	0.5983(2)	0.33765(18)	0.0764(7)
C11	0.0396(2)	0.66240(15)	0.44051(16)	0.0648(6)
C12	0.1536(2)	0.63482(17)	0.54050(18)	0.0696(7)
C13	0.2458(2)	0.54520(17)	0.53640(17)	0.0713(7)
C14	−0.0469(3)	0.8073(2)	0.5433(2)	0.0924(10)

Note. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

in similar azo compounds participate in either both inter- and intramolecular [18–22] or only one intermolecular hydrogen bond [23, 24]. Whereas here atom O1 participates in two different intermolecular hydrogen bonds, so that the fibroid structure occurs (see Fig. 2). However, the presence of different intermolecular hydrogen bonds associated with oxygen atoms in the azo compounds may lead to form tetrameric azo compounds [25]. Azo compounds have been used for dyeing textile and fibers [27]. The crystal structure determination of the title compound encourages it to be of fibroid dye character in the solid state.

Besides intermolecular hydrogen bonds, a remarkable π–π stacking (face-to-face) interaction associated with 2-methyl phenol ring (*fractional centroid coordinates:* 0.13395(8), 0.57250(7), 0.43713(7)) and two edge-to-face interactions associated with methoxy phenyl ring (*fractional centroid coordinates:* 0.53047(8), 0.16628(6), 0.36384(6)) were observed in the crystal structure. The centroid–centroid distance of the π–π stacking interaction is 3.7921(12) Åwith the symmetry code ($-x$, $1-y$, $1-z$). H···Cg(π-ring) distances of the two edge-to-face interactions, C1–H1b···Cg(π-ring) and C12–H12···Cg(π-ring), are 2.96(3) and 3.37(2) Åwith their respective symmetry operations ($1-x$, $-y$, $1-z$) and ($1-x$, $1-y$, $1-z$).

Computational study

The *trans* symmetry imposed semiempirical PM3 molecular orbital calculations were carried out in order to define the conformational flexibility of the title molecule as a function of the selected degrees of torsional freedom T(N1–N2–C8–C13) and T(N2–N1–C6–C5) (see Fig. 3) and to recognize the packing effects on molecules. Some selected geometrical parameters experimentally obtained and theoretically calculated are listed in Table 4.

When the X-ray structure of the title compound is contrasted with its PM3 optimized counterpart (see Fig. 4), a conformational discrepancy is observed between them, especially in the relative orientation of the substituted rings in the title compound. Although the optimized structure is nearly planar, X-ray structure has some geometrical differences from its planar geometry. According to X-ray study, dihedral angle between 2-methyl phenol and methoxy phenyl rings is 16.01(9)°, whereas the dihedral angle in the PM3 optimized geometry of the title compound is −3.25°. In addition, the respective values of the selected degrees of torsional freedom, T(N1–N2–C8–C13) and T(N2–N1–C6–C5), are 164.15(17)° and −176.2° in X-ray structure, whereas the corresponding values in PM3 optimized geometry are

Table 3 Hydrogen bonding geometry for the title compound

D—H···A	D—H (Å)	H···A (Å)	D···A (Å)	∠D—H···A
O1—H1···N1[a]	0.91(2)	2.01(2)	2.9043(18)	166(2)
C14—H14a···O1[b]	0.93(3)	2.43(2)	3.238(3)	145(2)

Note. D: donor, A: acceptor. Symmetry transformations used to generate equivalent atoms.

[a] $1-x$, $-0.5+y$, $0.5-z$.

[b] x, -0.5 $-y$, $-0.5+z$.

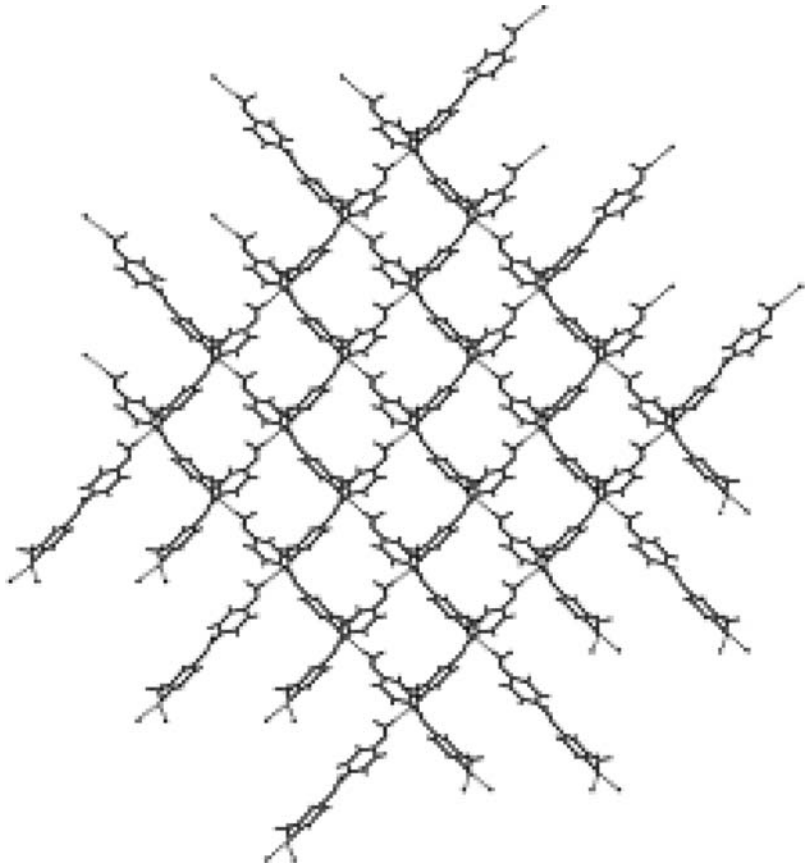


Fig. 2 Crystal packing view from *c*-axis showing crossed fibers of the compound in the solid state

178.50° and 178.52°. When C6–N1–N2–C8 torsion angle is considered, the distortions in X-ray and PM3 optimized structure from exact *trans* configuration of the title compound are found to be 3.03(15)° and 0.02°, respectively. Energy differences between the most favorable and unfavorable conformer, which arises from rotational potential barrier calculated with respect to the two selected torsion angles, are calculated as 3.90 kcal/mol when both selected degrees of torsional freedom are considered. It can be stated that both selected torsion angles lead to the same behavior in molecular energy profile (see Fig. 3). Moreover, there is no remarkable steric hindrance during the rotations around the selected torsion angles.

The molecular energy can be divided into bonded and nonbonded contributions. The bonded term is independent of changes in torsion angles. The nonbonded energy is further separated into torsional and steric terms. When the fact that there is no intramolecular hydrogen bond in the title compound is considered, it is inferred from the computational results that the most stable conformer of the title compound is primarily determined by the nonbonded torsional energy term affected by packing

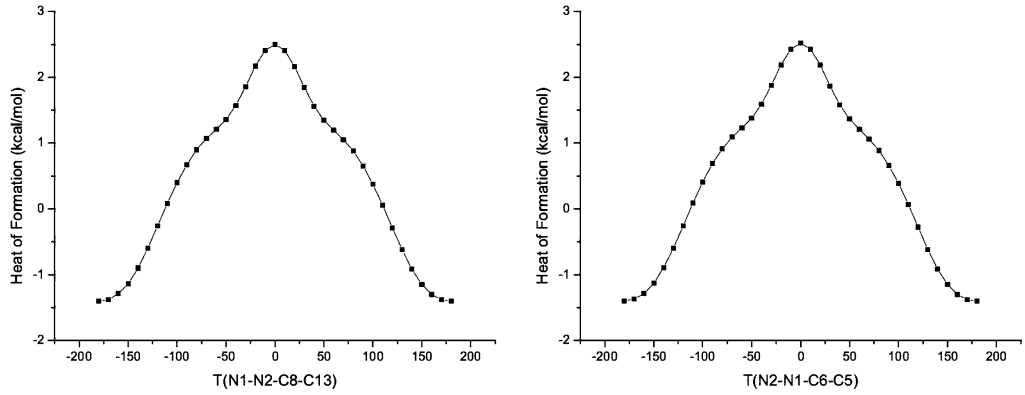


Fig. 3 Molecular energy profiles of the optimized counterpart of the title compound against the selected degrees of torsional freedom

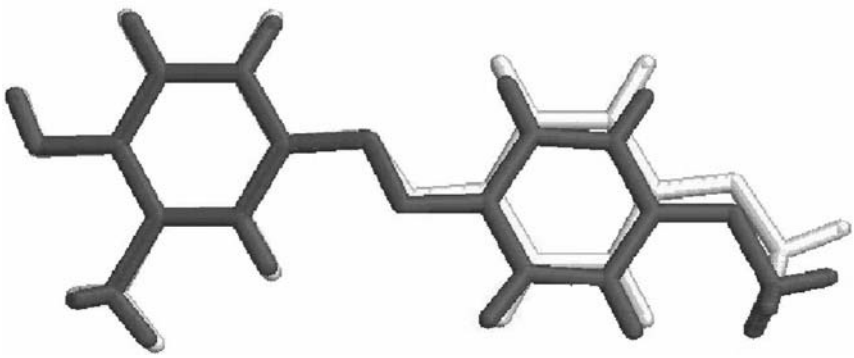


Fig. 4 Superimposition of the X-ray structure of the title compound (*dark*) and its PM3 optimized counterpart

of the molecules which satisfied the space group symmetry operations.

In the solid state, hydrogen bonds are practically never in an optimal geometry, and are always influenced by their environment. There are numerous effects from their close and also from their remote surrounding that may considerably increase or decrease hydrogen bond energies ("crystal-field effects"). In spite of these, when heats of formation of two different dimers of the title compound constructed by O–H···N and C–H···O type intermolecular hydrogen bonds are contrasted with the total heats of formation of two free monomers, the forming energies of O–H···N and C–H···O type intermolecular hydrogen bonds are found to be 1.93 and 1.68 kcal/mol, respectively. It is inferred from the calculations about the dimeric structures that O–H···N type hydrogen bond is relatively stronger than the other one.

In conclusion, X-ray structure is slightly different from its PM3 optimized counterpart, and the crystal structure is stabilized by O–H···N and C–H···O type hydrogen bonds besides π–π stacking and edge-to-face interactions. Crystal packing of the title compound is dominated only by intermolecular hydrogen bonds formed during preparation or crystallization. These hydrogen bonds supply leading contribution to the stability and to the order of the crystal structure, and are presumably responsible for the discrepancies between the X-ray and PM3 optimized structures of the compound.

Table 4 Some geometrical parameters in X-ray and PM3 optimized structure of the title compound

Parameter	X-ray	PM3
Bond lengths (Å)		
O1–C3	1.357(2)	1.367
O2–C11	1.353(2)	1.378
O2–C14	1.425(3)	1.406
C1–C2	1.503(3)	1.486
Bond angles (°)		
C11–O2 –C14	117.09(17)	117.58
N2–N1–C6	113.11(13)	119.91
N1–N2–C8	114.58(14)	119.86
N1–C6–C7	124.56(15)	124.36
N2–C8–C13	115.37(16)	115.35
Torsion angles (°)		
N2–N1–C6–C5	176.21(16)	178.52
C14–O2–C11–C12	− 4.1(3)	− 0.03
C1–C2–C3–O1	1.2(3)	0.02
C2–C3–O1–H1	− 176.6(15)	− 179.98

Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 292856. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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