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Anomeric effects in non-carbohydrate compounds: conformational differences between the oxazolidine rings of a cis-fused bicyclic system

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Dedicated to Professor R.U. Lemieux, Emeritus Professor of the University of Alberta, Edmonton, Canada, on the occasion of his 80th birthday

Abstract

Tris(hydroxymethyl)aminomethane (Tris) can react with benzaldehyde (1:2 molar ratio) to produce *cis*-2,8-diphenyl-5-hydroxymethyl-1-aza-3,7-dioxabicyclo[3.3.0]octane, the structure of which has been confirmed by nuclear magnetic resonance spectroscopy and X-ray crystallography. The crystal structure showed that both oxazolidine rings A and B are puckered in opposite directions. Ring A exists in an E_3 envelope form with O-3 noticeably down (0.65 Å) the plane of the remaining atoms, whereas ring B adopts the ^7E envelope conformation with the O-7 atom displaced up from the mean reference plane by 0.70 Å. Comparison of bond angles and bond distances showed that both oxazolidine rings A and B exhibit cross endo-anomeric effects resulting from electron delocalization over the bond sequence O-3–C-2–N-1–C-8–O-7.

Keywords: X-ray structure; Conformation; Cooperative anomeric effect; Oxazolidine

1. Introduction

Cyclohexane rings bearing an electronegative group, OR, SR, halogen, favor conformations having these groups in an equatorial orientation. However, in tetrahydropyran or tetrahydrofuran rings substituted at C-2, these polar substituents have a preference for the axial orientation. This property, of stereoelectronic origin, was named the anomeric effect by Lemieux in 1958 [1a,b]. This discovery was made possible by the advent of ^{1}H NMR spectroscopy for the establishment of conformational preferences and relative configurations at chiral centers [1c].

The anomeric effect is now recognized as one of the most important factors of conformational analysis of saturated heterocyclic systems. This effect is not limited to sugars

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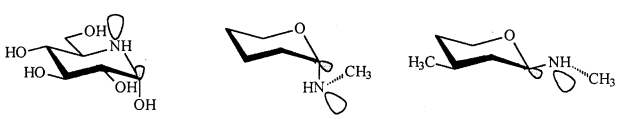
and tetrahydropyran rings. It is also observed in other heterocycles, as well as in acyclic structures, providing a motif C–Y–C–X (where Y is an heteroatom with an appropriately oriented unshared pair of electrons and X an electronegative group) is present, and many reviews have summarized the phenomenon [2–8].

The early proposal for the existence of a stereoelectronic effect based on dipole–dipole interaction [9] failed to explain the changes in molecular geometry (bond distances and bond angles) observed in alkyl glycosides [10] and glycosyl halides [11]. X-ray crystallographic studies have revealed that the C-1–O-1 (or C-1–X) bond is slightly longer (weaker) in α anomers than in β analogs and that the C-1–O-5 bond is shorter (stronger). At the same time, the bond angle O-5–C-1–O-1 (or O-5–C-1–X) in the α anomer is greater than in the β anomeric counterpart.

The stereoelectronic rationalization of these structural modifications arose from the pioneering work of Altona and co-workers [11,12] who suggested that the stabilization of the axial anomers was associated to electron transfer from the antiperiplanar lone-pair orbital on ring oxygen to the σ* antibonding orbital of the C-1–O-1 (or C-1–X) bond. Electron transfer results in the lengthening of the exocyclic bond, contraction of the C-1–O-ring bond by increasing its double-bond character and opening of the O-5–C-1–O-1 (or X) angle as compared with its normal tetrahedral value.

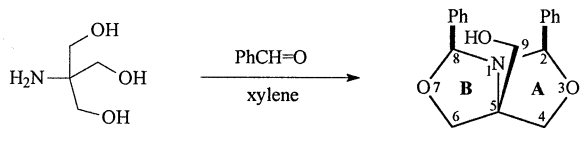
Convincing evidence of the generality of anomeric effects postulated by Lemieux in 1971 [8] is provided by the alkaloid nojirimycin (**1**) which contains a C–N–C–O moiety. Nitrogen being a better electron donor and oxygen a better electron acceptor, one can predict the axial conformer **1a** to be substantially favored over the equatorial one as a result of the manifestation of an endo-anomeric effect [1–4]. Indeed the α/β ratio determined by ^{1}H NMR spectroscopy was shown to be 63:37 as compared with 36:64 for D-glucopyranose [13].

Confirmation of such behavior can be found in the work of Booth and Khedair [14a] based on ^{13}C and ^{1}H NMR studies of the anomeric equilibrium constants of two-substituted tetrahydropyrans **2** and **3** as compared with the cyclohexane analogs. Conformations **2a** and **3e** (Scheme 1) were found to predominate as a result of an antiperiplanar $n \rightarrow \sigma^*$ interaction of the exocyclic nitrogen lone-pair with the antibonding orbital of the endocyclic carbon–oxygen bond. These findings provide a clear illustration of the exo-anomeric effect [15], a subject that has become of major importance in predicting the orientation of the aglycon of glycosides [14b].



1a **2a** **3e**

Scheme 1.



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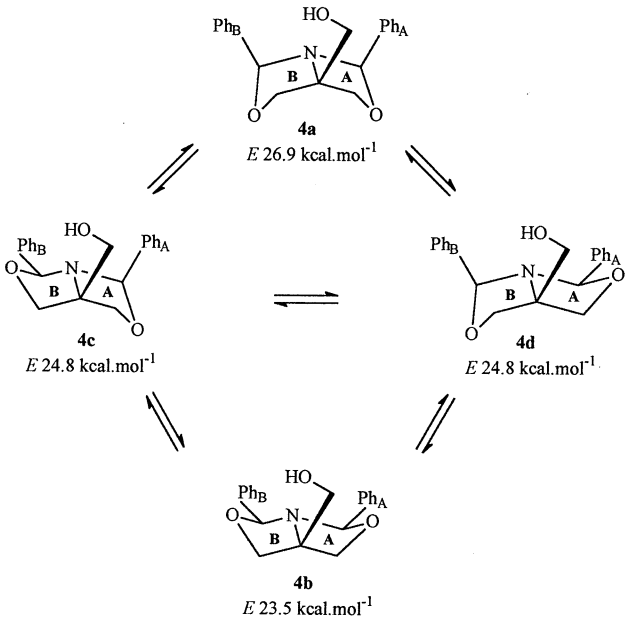
Scheme 2.

2. Results and discussion

During the course of research aimed at developing strategies for the protection, the deprotection and functionalization of tris(hydroxymethyl)aminomethane (Tris), we prepared 2,8-diphenyl-5-hydroxymethyl-1-aza-3,7-dioxabicyclo[3.3.0]octane (**4**) [16], the stereochemistry of which was never established (Scheme 2).

The ^{1}H NMR spectrum of compound **4** in $CDCl_3$ displayed a two-proton singlet at 5.56 ppm for the C-2 and C-8 benzyl protons together with a well-resolved four-proton quartet (AB system) at 4.00 and 3.88 ppm (J 8.8 Hz), respectively. The identity of the benzyl protons and the presence of an AB pattern for the methylene protons at C-4 and C-6 reflect the perfect symmetry of the molecule and thereby confirm that **4** is the meso diastereoisomer.

An examination of molecular models showed that: (i) cis-fusion of the oxazolidine



Scheme 3.

rings was highly favored over the considerably more strained trans-fusion; (ii) compound **4** can exist in a number of flexible conformations upon pseudorotation occurring at each oxazolidine ring as seen in Scheme 3; (iii) only conformers **4a** and **4b** can account, a priori, for the observed NMR spectrum.

For several reasons [including: (i) the existence of two identical five-membered rings; (ii) the presence of two consecutive C–O–C–N motifs sharing the same nitrogen atom as electron donor; (iii) the symmetry of the molecule], we considered compound **4** to be a unique model to study intracyclic stereoelectronic effects. We anticipated that the endo-anomeric effect will predominate. Therefore, if ring A for example displays a conformation prone to allow delocalization of the nitrogen lone-pair orbital to the antibonding orbital σ* of the C-2–O-3 bond, this will have several consequences on both oxazolidine rings in terms of: (i) conformation; (ii) bond distances; (iii) bond angles and possibly; (iv) reactivity.

Molecular modeling using the GENMOL program [17] allowed us to evaluate — regardless of any contribution from the anomeric effects — the energies of conformers **4a**, **4b**, **4c** (**4d**), to be 26.9, 23.5 and 24.8 kcal mol^{-1}, respectively. It is self-evident that conformer **4d**, arising from **4b** upon ring inversion of the oxazolidine B, would be identical in all respect to conformer **4c**, except for the relative orientation of the phenyl groups. Both are pseudo-equatorial in **4b** whereas Ph(A) is pseudo-axial in **4c** and Ph(B) pseudo-axial in **4d**.

Considering the small energy difference (1.3 kcal mol^{-1}) between **4b** and **4c** (**4d**) and the fact that the latter should be stabilized by the anomeric effects, we speculated that either **4c**, or more likely a rapid equilibrium between **4c** and **4d**, should represent the structure of compound **4** in solution.

It has been shown that a five-membered ring orients polar substituents at the anomeric center in axial or pseudo-axial orientation much more strongly than the six-membered pyranose ring [18]. Moreover, the stabilization arising from an $n \rightarrow \sigma^*$ conjugation should be more pronounced in a C–N–C–O–C motif than in its C–O–C–O–C counterpart. For all these reasons, we assumed the conformer **4c** (**4d**), in which either C-2–O-3 (or C-8–O-7) bond is antiperiplanar to the axial lone pair on nitrogen, should be strongly favored. Confirmation of such assumptions was provided by the X-ray crystal-structure of compound **4** (crystal data for **4** are given in Table 1).

3. Crystal structure of 4

The positional and equivalent thermal isotropic parameters for the non-hydrogen atoms are listed in Table 2. Selected bond distances and bond angles as well as selected torsional angles are given in Tables 3 and 4, respectively. The X-ray crystal-structure of **4** is consistent with what was anticipated from molecular modeling. The overall geometry of the molecule is of the bicyclic type with two cis-fused five-membered rings (see Fig. 1). The two phenyl groups are in a cis configuration: pseudo-axial for that linked to carbon-2 and pseudo-equatorial for that attached to carbon-8. The hydroxymethyl group C-9–O-10 is syn-periplanar to the pseudo-axial nitrogen lone pair. The two five-membered rings are significantly puckered in opposite directions. Thus the C-2–O-3–C-4 plane makes a dihedral angle of 141.2° with the C-2–N-1–C-5–C-4 mean

plane. On the other hand, the C-6–O-7–C-8 plane and the C-8–N-1–C-5–C-6 mean plane make a dihedral angle of 136.2°. As expected, the dihedral angle between C-2–N-1–C-5–C-4 and C-8–N-1–C-5–C-6 mean planes is close to 120° (119.4°). The packing of the molecule results from usual van der Waals contacts (mainly between aromatic hydrogen atoms and aromatic carbon atoms) and also from a long (1.907(2) Å) hydrogen bond between the hydroxyl group O-10–H and the O-7 atom of the neighboring molecule $(1/2-x, 1/2+y, 1/2-z)$. The latter can be compared with the short H···O distance found in ice (1.74 Å), which is probably the lowest limit for this kind of interaction.

The most significant crystal data in relation to the impact of the anomeric effects on the structure of compound **4**, are summarized in Fig. 2. These call for the following remarks: (i) the oxazolidine ring A adopts an envelope conformation very close to the theoretical envelope form E_3. Oxygen-3 was found to be noticeably down (0.65 Å) the plane, defined by atoms C-2–N-1–C-5, whereas C-4 deviated slightly (0.12 Å) from the above reference plane producing a torsion angle C-4–C-5–N-1–C-2 of 5°. This three-dimensional structure allows $n \rightarrow \sigma^*$ delocalization of electrons as confirmed by the contraction of the N-1–C-2 bond (1.458 Å) compared with 1.491 and 1.477 Å for N-1–C-5 and N-1–C-8 bonds, respectively; (ii) of special interest are the differences in bond angles involving the bridgehead nitrogen. The C-2–N-1–C-8 angle is significantly greater (112.9°) than either C-2–N-1–C-5 (105.4°) or C-8–N-1–C-5 (105.8°). Indeed, the manifestation of an endo-anomeric effect in ring A is also illustrated by the difference in bond angles: 106° for O-3–C-2–N-1 instead of 103.3° for O-7–C-8–N-1; (iii) in contrast, ring B exists in a ^7E envelope conformation characterized by atoms O-7 and C-6 displaced up from the plane C-8–N-1–C-5 by 0.70 and 0.12 Å, respectively (torsion angle

Table 1
Summary of crystal data, intensity measurements and refinement, for compound **4**

Formula	$C_{18}H_{19}NO_3$
Crystal system	monoclinic
Space group	$P2_1/n$ (no. 14)
a (Å)	6.258(1) [a]
b (Å)	9.465(1)
c (Å)	25.722(4)
β (°)	94.445(13)
V (Å^3)	1518.9(4)
Molecular weight	297.35
Z	4
D_{calcd} at 177 K (g cm^{-3})	1.300
D_{measd} at 293 K (g cm^{-3})	1.27(3)
Crystal size (mm^3)	$0.40 \times 0.19 \times 0.08$
Crystal color	colorless
Recrystallization solvent	diethyl ether
Mp (°C)	91–92
Method of data collection	ω–θ
Radiation (graphite monochromated)	Mo K_α ($\lambda = 0.71069$ Å)
μ (cm^{-1})	0.87
2θ Limits (°)	4–60
No. of unique reflections	4080
No. of observed reflections	2422
Final no. of variables	209
R_1 for 729 observed	0.0434
σ Cut-off	$F_o > 4\sigma(F_o)$
wR_2 (on F^2)	0.0960
Goodness-of-fit	0.804
Residual electron density	0.23 (−0.23)

[a] Parameters measured at 177 K.

Table 2
Fractional atomic coordinates for the non-hydrogen atoms and the hydroxyl-hydrogen atom, and the corresponding isotropic thermal parameters

Atom	x/a	y/b	z/c	U_{eq}
N-1	0.5052(2)	0.46588(12)	0.15387(4)	0.0198(3)
C-2	0.6645(2)	0.4957(2)	0.11686(6)	0.0221(3)
O-3	0.8482(2)	0.54919(11)	0.14701(4)	0.0270(2)
C-4	0.7593(2)	0.6408(2)	0.18394(6)	0.0272(3)
C-5	0.5531(2)	0.5663(2)	0.19786(5)	0.0212(3)
C-6	0.5830(3)	0.4694(2)	0.24519(6)	0.0288(4)
O-7	0.4704(2)	0.3433(1)	0.22875(4)	0.0274(2)
C-8	0.5280(2)	0.3232(2)	0.17688(6)	0.0236(3)
C-9	0.3684(2)	0.6672(2)	0.20216(6)	0.0270(3)
O-10	0.4377(2)	0.7732(1)	0.23872(4)	0.0370(3)
H	0.3130	0.8015	0.2535	0.040
C-11	0.3838(2)	0.2158(2)	0.14933(5)	0.0231(3)
C-12	0.1725(2)	0.2494(2)	0.13338(6)	0.0278(3)
C-13	0.0419(3)	0.1492(2)	0.10844(6)	0.0354(4)
C-14	0.1196(3)	0.0163(2)	0.09876(7)	0.0393(4)
C-15	0.3294(3)	−0.0182(2)	0.11416(6)	0.0394(4)
C-16	0.4599(3)	0.0820(2)	0.13991(6)	0.0314(4)
C-21	0.5837(2)	0.5988(2)	0.07496(5)	0.0227(3)
C-22	0.3723(3)	0.5972(2)	0.05433(6)	0.0279(3)
C-23	0.3045(3)	0.6886(2)	0.01448(6)	0.0338(4)
C-24	0.4459(3)	0.7828(2)	−0.00497(6)	0.0374(4)
C-25	0.6566(3)	0.7842(2)	0.01491(6)	0.0397(4)
C-26	0.7250(3)	0.6926(2)	0.05450(6)	0.0324(4)

Table 3
Selected bond distances (Å) and bond angles (°)

N-1–C-2	1.458(2)
N-1–C-5	1.491(2)
N-1–C-8	1.477(2)
O-3–C-2	1.429(2)
O-3–C-4	1.430(2)
O-7–C-6	1.433(2)
O-7–C-8	1.421(2)
C-4–C-5	1.537(2)
C-5–C-6	1.524(2)
C-5–C-9	1.510(2)
C-9–O-10	1.420(2)
C-2–C-21	1.512(2)
C-8–C-11	1.500(2)
C-8–N-1–C-5	105.8(1)
C-5–N-1–C-2	105.4(1)
C-8–N-1–C-2	112.9(1)
N-1–C-2–O-3	106.0(1)
N-1–C-2–C-21	112.5(1)
O-3–C-2–C-21	111.6(1)
C-2–O-3–C-4	103.7(1)
O-3–C-4–C-5	104.7(1)
C-4–C-5–N-1	103.8(1)
C-4–C-5–C-6	114.1(1)
C-4–C-5–C-9	112.8(1)
N-1–C-5–C-6	103.2(1)
C-6–C-5–C-9	111.7(1)
C-9–C-5–N-1	110.4(1)
C-5–C-6–O-7	103.8(1)
C-6–O-7–C-8	103.5(1)
O-7–C-8–N-1	103.3(1)
O-7–C-8–C-11	110.3(1)
N-1–C-8–C-11	113.2(1)
C-5–C-9–O-10	107.4(1)

C-6–C-5–N-1–C-8 +4°5), and by a small difference in bond distance between O-7–C-8 and O-3–C-2; (iv) from the above considerations, one can conclude that the conformations of both oxazolidine rings A and B manifest cross endo-anomeric effects resulting from delocalization of electrons over the bond sequence O-3–C-2–N-1–C-8–O-7. The reverse motion of electrons in ring B can be considered if the nitrogen atoms becomes — as a result of the above $n \rightarrow \sigma^*$ hyperconjugation occurring in ring A — a better electron acceptor than it is normally expected to be. Indeed, the geometry of the molecule allows antiperiplanar $n \rightarrow \sigma^*$ interaction between the pseudo-equatorial sp^3 lone-pair on oxygen O-7 with the N-1–C-8 antibonding orbital σ^*.

4. Conclusions

The most important conclusions follow: (i) compound **4** is very well suited to study intracyclic stereoelectronic effects; (ii) the latter govern the conformation of both oxazolidine rings in this bis(oxazolidine) system; (iii) the precision of the crystallographic data cast no doubt on the reality of a cooperative stereoelectronic effect along the –O–C–N–C–O– grouping.

5. Experimental

Synthesis

cis-*2,8-Diphenyl-5-hydroxymethyl-1-aza-3,7-dioxabicyclo[3.3.0]octane* (**4**). Tris(hydroxymethyl)aminomethane (10 g, 82.5 mmol) and benzaldehyde (16.8 mL, 165 mmol) were poured into a 500 mL round flask containing 100 mL of hot (80–100 °C) xylene, fitted with a Dean and Stark apparatus. The mixture was refluxed until the liquid recovered in the graduated tube had become clear (4–5 h). The xylene was removed under diminished pressure, the oily residue dissolved in hot diethyl ether followed by filtration to remove the unreacted material (Tris). The filtrate was evaporated to dryness and the solid residue was purified by recrystallization from diethyl ether. Pure **4** was obtained as a white solid (15.9 g, 65%) mp 91–92 °C; lit. [16] 93–95 °C.

The minor trans-isomer was obtained after silica gel column chromatography (1:1 diethyl

Table 4
Dihedral angles (°) between the mean planes in the bicyclic core of the molecule *

Atoms defining the plane	C-2–O-3–C-4	N-1–C-2–C-4–C-5	N-1–C-8–C-6–C-5	C-6–O-7–C-8
Equation	a	b	c	d
Dihedral angle	141.2	119.4	136.2	

* Equations of the planes: (a) $0.602x+7.241y-16.519z=2.059$; (b) $3.372x+6.752y-10.416z=0.131$; (c) $6.208x-0.161y-5.177z=2.292$; (d) $4.763x-5.204y+7.303z=2.125$.

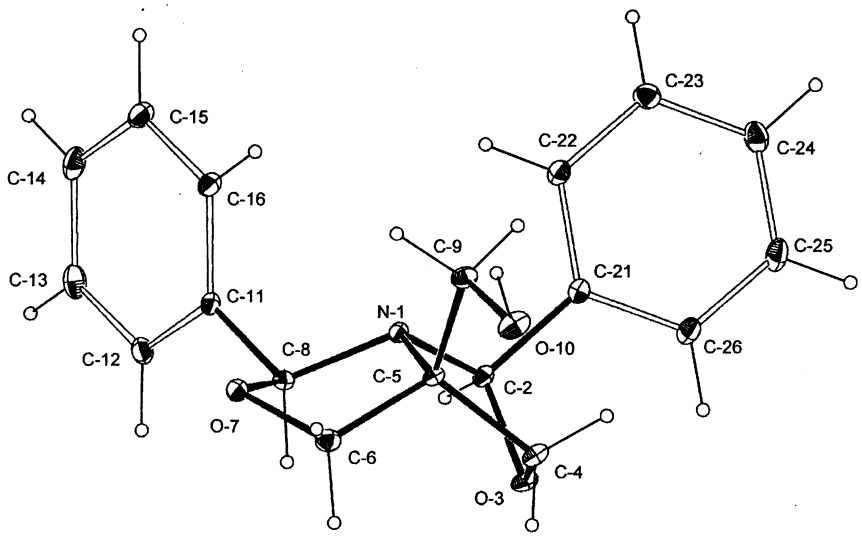


Fig. 1. ORTEP view for compound **4**. The thermal ellipsoids are drawn at the 30% probability level.

ether–petroleum ether, v/v) of the mother liquors as a white solid (2.0 g, ≈8%) mp 104–106 °C.

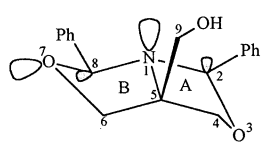
Molecular modeling.—The molecular modeling was achieved on an Impact 10000 Silicon Graphics computer with the aid of the GENMOL program using the soft-proton option [17].

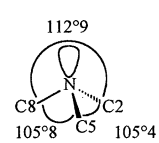
X-ray diffraction structure determination.—Suitable single crystals of **4** were grown from diethyl ether solution by slow evaporation. The crystal data and a summary of experimental data are given in Table 1.

A small block (length 0.4 mm) of **4** was cut from a needle, secured at the end of a glass pin with thick mineral oil and immersed in a flow of nitrogen at 177 K on a CAD-4 automated diffractometer with graphite-monochromatized Mo K_α radiation ($\lambda = 0.71069$ Å).

X-ray data collection.—Lattice constants (Table 2) came from a least-squares refinement of 25 reflections obtained in the range $11.9° < 2\theta < 26.3°$. The intensities were monitored after intervals of 60 min; no significant change in these intensities occurred. The structure amplitudes were obtained after the usual Lorentz and polarisation reductions. No absorption corrections were made.

Structure determination and refinement.—Direct methods (SHELXS-86 program [19]) were used to solve the structure with 4080 independent data. The whole set of non-hydrogen atoms was obtained through a single calculation. After five cycles of least-squares refinement with isotropic thermal parameters to all atoms, the hydrogen atoms were positioned by calculation (SHELXL-93 program [20]) and included in the further stages of the refinement (riding model). Anisotropic thermal parameters were given to all non-hydrogen atoms and the position of the hydroxyl hydrogen atom was located in a difference Fourier map. The coordinates of this hydrogen atom were kept fixed throughout the calculation. The refinement converged at the final R_1 value of 0.0434 for 2422 $F_o > 4\sigma(F_o)$, and $wR_2 = 0.0960$ for all data. The final atomic coordinates with the associated thermal





d (Å)

N-1—C-2 : 1.458 (2)
C-2—O-3 : 1.429 (2)
C-4—O-3 : 1.430 (2)
N-1—C-5 : 1.491 (2)
N-1—C-8 : 1.477 (2)
C-8—O-7 : 1.421 (2)
C-6—O-7 : 1.433 (2)

Angles (°)

C-2–N-1–C-8 : 112.9 (1)
C-8–N-1–C-5 : 105.8 (1)
C-2–N-1–C-5 : 105.4 (1)
O-3–C-2–N-1 : 106.0 (1)
O-7–C-8–N-1 : 103.3 (1)

Fig. 2. Selected crystal data for compound **4**.

parameters are listed in Table 2. The labeling scheme is given in Fig. 1.

6. Supplementary material

Full crystallographic details have been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 139898). These data may be obtained on request from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (tel.: +44-1223-336408; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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