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RESEARCH ARTICLE

Synthesis and characterisation of two new bicyclic oxazolidines and investigation of their optoelectronic properties using density functional theory

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Abstract: This paper presents a facile synthetic route to synthesise two new bicyclic oxazolidine compounds 3,5-bis(4-chlorophenyl)-7a-methyldihydro-1H-[1,3]oxazolo[3,4-c][1,3] oxazole (1) and 3,5-bis(2-methoxyphenyl)-7a-methyldihydro-1H-[1,3]oxazolo[3,4-c][1,3]oxazole (2). The condensation reaction between 2-amino-2-methylpropane-1, 3-diol ($ampdH_2$) and choloro- and methoxy- substituted aromatic aldehyde yielded the heterocyclic bicyclic compounds (1) and (2), respectively. The compounds are characterised by FT-IR and ^{1}HNMR spectroscopy and structures are conclusively determined by single crystal X-ray diffraction analysis. The ground state geometries are optimised by using density functional theory (DFT) at B3LYP/6-31G** level of theory to compare the geometric parameters (bond lengths, bond angles and torsion angles) with the X-ray crystallographic data. The computed geometric parameters are in good agreement with the experimental data. To shed light on the electronic and photophysical properties, DFT/B3LYP/6-31G** and time dependent DFT have been applied, respectively. Intra-molecular charge transfer has been observed in both the compounds. The absorption wavelengths are calculated with and without the solvent (acetone, acetonitrile, dimethylformamide, dimethyl sulfoxide and methanol) at TD-B3LYP/6-31G** level of theory.

Keywords: Density functional theory, optoelectronic properties, synthesis, time dependent density functional theory.

INTRODUCTION

Heterocyclic compounds have attained immense interest due to their wide range of applications in modifiers, additives, cosmetics, plastics and antioxidants (Martins *et al*., 2009). The cyclic compounds containing carbon, hydrogen and heteroatoms have exhibited diverse physical, chemical and biological properties (Martins *et al*., 2008). Oxazolidine is a class of cyclic compounds, which has displayed wide range of biological properties such as antibacterial, antitumor and antimicrobial activities (Sriharsha & Shashikanth, 2006). These compounds are employed extensively as curing agents for resins (Swedo & Green, 2004), synthetic intermediates (Huguenot & Brigaud, 2006), chiral auxiliaries, and precursors for synthetically and pharmaceutically important amino alcohols present in natural products (Kim *et al*., 2003). Oxazolidines are synthesised by several routes, however, the most direct route is the condensation of aminoalcohol and aldehyde or ketones forming mono oxazolidines (Kang *et al*., 2005). The synthesis of bicyclic bisoxazolidines has been the least explored area to date (Saiz *et al*., 2011). 2-amino-2-methylpropane-1,3-diol ($ampdH_2$) is a versatile compound possessing three

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nucleophiles, which is considered as a suitable substrate for cycloaddition reactions giving five membered saturated heterocyclic compounds (Peera & TomLinson, 2015). Two equivalents of the same aldehyde are used in both steps to form heterocyclic compounds (Bergmann, 1953). Previously, we reported $ampdH_2$ as a ligand to synthesise tetranuclear lanthanide coordination complexes exhibiting single molecule magnet (SMM) behaviour (Abbas *et al*., 2012).

Herein, we report the synthesis of new bicyclic oxazolidines obtained by the reaction of $ampdH_2$ with p-chloro-benzaldehyde and o-methoxy benzaldehyde. The structures of resulting compounds were elucidated by spectroscopic techniques as well as single crystal X-ray diffraction. The ground state geometers were optimised using density functional theory (DFT) at B3LYP/6-31G** level of theory to compare the geometric parameters (bond lengths, bond angles and torsion angles) with the X-ray crystallographic data.

METHODOLOGY

All chemicals and reagents were purchased from Acros, Germany with 98 % purity and used without further purification. The elemental analyses (C, H, N) were performed using an Elementar Vario EL analyser. FT-IR (450 – 4000 cm) spectra were recorded on a Thermo-nicolet 6700, USA FT-IR spectrometer. ^{1}HNMR spectra were recorded on a Bruker Avance 300 MHz spectrometer and calibrated to residual solvent peaks. The electronic spectra were recorded on Labomed UVD2300 UV/Vis spectrophotometer. Single crystal XRD data were collected on an Oxford-Diffraction diffractometer, equipped with a charge - coupled device (CCD) area detector and a graphite monochromator utilising MoK-α radiation (λ = 0.71073 Å).

Synthesis of 3,5-bis(4-chlorophenyl)-7a-methyldihydro-1H-[1,3]oxazolo[3,4-c][1,3]oxazole (1)

To a well stirred solution of chlorobenzaldehyde (2 mmol in 10 mL absolute ethanol) a solution of 2-amino-2-methyl-1,3-propandiol (1 mmol in 10 mL ethanol) was added and refluxed for 3 h. The resulting mixture was cooled at room temperature and kept undisturbed. Colourless needle like crystals of compound (1) separated out overnight. Yield 87 %: Anal. Calc. for $C_{18}H_{17}Cl_2NO_2$: C, 61.72 H, 4.89 N, 3.99 found: C,61.67 H, 4.81 N, 3.87. FT-IR (KBr cm^{-1}) 2954 (C-H), 3097 (C-H str), 1489 (C=C), 1375 (C-H), 1142 (C-N), 1074 (C-O). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33-7.27 (2H, m), 7.26-7.18 (4H, m), 7.13-7.08 (2H, m), 5.58 (1H, s), 5.18 (1H, s), 4.10 (1H, d), 3.88 (1H, d), 3.85 (1H, d), 3.65 (1H, d), 1.45 (3H, s).

Synthesis of 3,5-bis(2-methoxyphenyl)-7a-methyldihydro-1H-[1,3]oxazolo[3,4-c][1,3]oxazole (2)

To a well stirred solution of methoxybenzaldehyde (2 mmol in 10 mL absolute ethanol) a solution of 2-amino-2-methyl-1,3-propandiol (1 mmol in 10 mL ethanol) was added and refluxed for 3 h. The resulting mixture was cooled and kept overnight. Colourless needle like crystals of compound (2) separated out. Yield 85 %: Anal. Calc. for $C_{20}H_{23}NO_4$: C, 70.36 H, 6.79 N, 4.10 found: C, 70.25 H, 6.68 N, 4.03. FT-IR (KBr cm^{-1}) 2970 (C-H), 3095 (C-H str), 1489 (C=C), 1158 (C-N), 1080 (C-O) ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78-7.68 (3H, m), 7.18-7.10 (2H, m), 6.99-6.83 (3H, m), 5.70 (1H, s), 5.69 (1H, s), 4.08 (1H, d), 3.86 (1H, d), 3.84 (1H, d), 3.62 (1H, d), 3.48 (3H, s), 3.34 (3H, s), 1.55 (3H, s).

Colourless needles of compound (1) suitable for analysis by X-ray diffraction (XRD) were obtained. All the measurements were performed using Mo-Kα radiation (λ = 0.71073 Å) at 100 K. Compound (1) crystallised in orthorhombic crystal system with space group *Pbca*, and the cell parameters were; a = 6.0577 (7) Å, b = 20.850 (2) Å, c = 25.272 (2) Å, V = 3191.9 (6) Å^3, Z = 8, crystal density = 1.458 mg m^{-3}, and absorption coefficient μ = 0.42 mm^{-1}. A total of 12362 reflections were measured (θ_{max} = 25.0), (R_{int} = 0.109) with 1839 reflections with $I > 2\sigma(I)$. The structure was solved by direct methods using SIR92 (Cascarano *et al*., 1994) and refined on F^2 using full-matrix least squares using SHELXL97 (Sheldrick, 1997). The final R indices of $R^1 = 0.059$ and $wR^2 = 0.156$ were obtained.

Compound (2) crystallised as monoclinic colourless needles with space group $P2_1/c$. All the measurements were performed using Mo-Kα radiation (λ = 0.71073 Å) at 100 K. Crystal cell parameters were; a = 11.2388 (7) Å, b = 9.8455 (7) Å, c = 15.5764 (10) Å, V = 1716.4 (2) Å^3, Z = 4, crystal density = 1.321 mgm^{-3}, and absorption coefficient μ = 0.09 mm^{-1}. A total of 7595 reflections were measured (θ_{max} = 25.0), (R_{int} = 0.027) with 2678 reflections with $I > 2\sigma(I)$.

Computational details

Among density functional theory (DFT) functionals B3LYP is a good choice, which provides the best description of the geometries (Gruhn *et al*., 2002; Sánchez-Carrera *et al*., 2006; Irfan *et al*., 2017a; b). In the present study, the ground state (S_0) geometries were optimised by DFT/B3LYP (Lee *et al*., 1988; Miehlich

et al., 1989; Becke, 1993) and 6-31G** basis set (Petersson *et al*., 1988). The frequency calculations were performed at the same level of theory. No imaginary frequency was noticed, which reveal that the optimised structures were reliable for further investigations. To compute the absorption wavelengths (λ_a), time dependent DFT was applied which has been proved as an efficient and accurate approach (Matthews *et al*., 1996; Irfan, 2013; 2014; Irfan *et al*., 2016). All the calculations were performed using Gaussian16 package (Frisch, 2016).

RESULTS AND DISCUSSION

Different synthetic strategies are opted to design bis oxazolidine compounds, which lead to obtain the target molecules using the same aldehyde in two steps. The important feature was to use the same carbonyl group in both steps of the synthesis as reported by Crab *et al*. (1973). Bicyclic oxazolidines were obtained by reaction of ampdH_2 with p-chloro-benzaldehyde and o-methoxy benzaldehyde. The cyclisation was carried out at elevated temperatures. Two equivalents of each aldehyde were used to obtain desired products. The stepwise synthesis of compounds (1) and (2) using ampdH_2 is given in Figure 1. The reactions were performed under thermodynamic control and monitored through thin layer chromatography (TLC). Both compounds were isolated as crystalline products in a single solvent; e.g. ethanol giving good yield and purity.

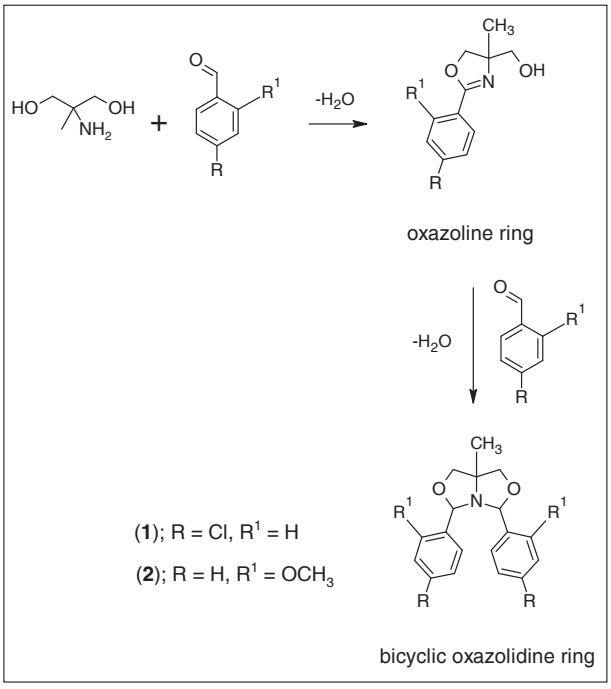

Figure 1: Reaction scheme for the synthesis of compounds (1) and (2)

Crystal structures analysis

The crystal structure of compounds (1) and (2) were solved and refined in orthorhombic and monoclinic crystal systems with space group *P*bca and $P2_1/c$, respectively. The crystal XRD data and refinement parameters of both compounds are given in Table 1 for better comparison.

The Oak Ridge thermal ellipsoid plot (ORTEP) view for compounds (1) and (2) are shown in Figure 2, while crystal structure unit cells are shown in Figure 3. The XRD analysis reveals that for compound (1), the centroids of two oxazoline rings (facing one another) are at a distance of 1.77 Å, whereas for compound (2) the distance between the centres of two oxazoline rings is 1.73 Å (Figure S1 - supplementary information). Bond lengths for compounds (1) and (2) are given in Tables 2 and 3, respectively.

Geometries

The geometrical parameters, bond lengths, bond angles, dihedral angles as well as dipole moments are presented in Table 4. The optimised geometrical parameters are in good agreement with the crystal structure parameters (atom numbering scheme, Figure S2 - supplementary information). By substituting the methoxy groups at phenyl rings, we observed the major change in N1-C7 bond length of compound (2), which shortened by 0.019 Å; the C7-N1-C14 bond angle decreases by 3.25° and torsion angles C4-C7-N1-C14/C4-C7-O2-C15 increases/decreases 33.27/72.07° compared to compound (1). The trend to increase the dipole moment was observed in the following order: compound (2) < compound (1). In compound (2), a smaller dipole moment was observed, which has the methoxy groups at phenyl rings. It was found that the introduction of the Cl groups at phenyl rings would boost up the dipole moment.

Electronic properties

Figure 4 illustrates the distribution pattern of the frontier molecular orbitals; highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs). In compounds (1) and (2), HOMO density is distributed on the phenyl ring and N atom of the central core while LUMO is distributed on both end phenyl rings. Most of the charge is transferred from central core

and N atom to phenyl moieties in compound (1), while in compound (2), charge is transferred from phenyl to phenyl moiety. Intra-molecular charge transfer (ICT) has been observed in both systems. The E_{gap} of these compounds were calculated at the B3LYP/6-31G** level of theory. The substitution of methoxy at phenyl ring increases the HOMOs and LUMOs energies compared to the Cl substituted derivative.

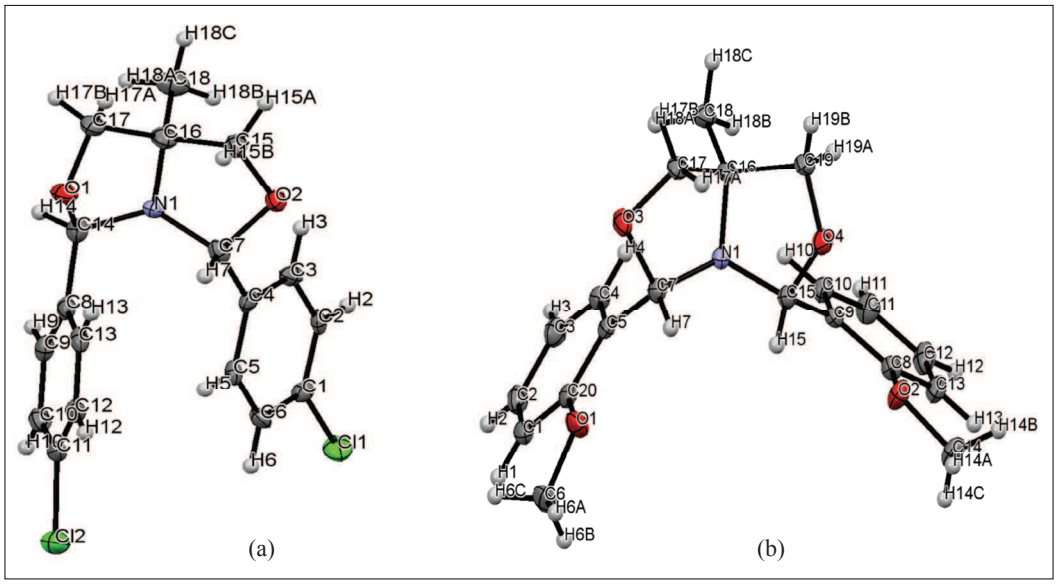

Figure 2: ORTEP plot of (a) compound (1) and (b) compound (2). Thermal ellipsoids are drawn at 50 % probability level

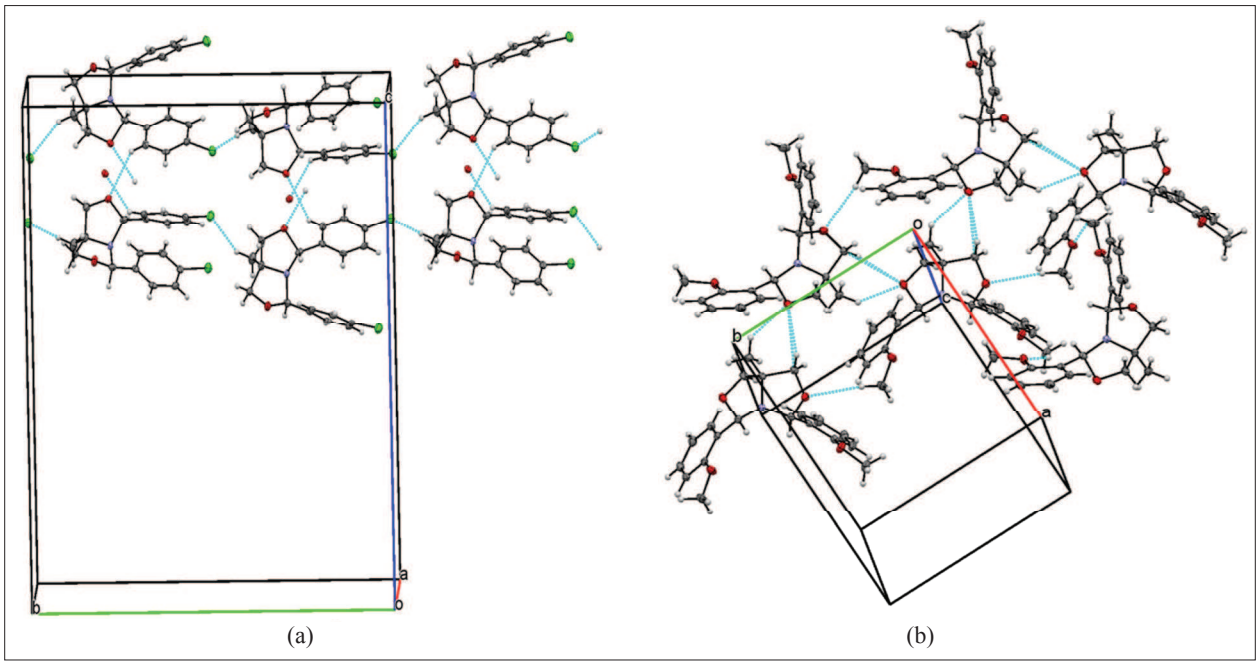

Figure 3: Crystal packing diagrams of (a) compound (1) and (b) compound (2). Hydrogen bond contacts are indicated with cyan dotted lines

Table 1: Summary of data collection and refinement parameters for compounds (1) and (2)

Compound	Compound (1)	Compound (2)
Formula	$C_{18}H_{17}Cl_2NO_2$	$C_{20}H_{23}NO_4$
Formula weight	350.23	341.39
Crystal size (mm)	0.15 × 0.03 × 0.02	0.13 × 0.06 × 0.02
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
a [Å]	6.0577 (7) Å	11.2388 (7) Å
b [Å]	20.850 (2) Å	9.8455 (7) Å
c [Å]	25.272 (2) Å	15.5764 (10) Å
V [Å^3]	3191.9 (6)	1716.4 (2)
Z	8	4
Density (Dx Mg m^{-3})	1.458	1.321
F(000)	1456	728
T [K]	100	100
μ [mm^{-1}]	0.42	0.09
θ range [°]	3.6 – 25.6	3.0 – 29.5
h	-7→7	-10→13
k	-24→22	-11→11
l	-28→30	-18→18
Measured reflections	12362	7595
Independent reflections	2803	3015
R_{int}	0.109	0.027
Parameters	216	234
S	1.02	1.07
Reflections with $I > 2\sigma(I)$	1839	2678
$R[F^2 > 2\sigma(F^2)]$	0.059	0.040
$wR(F^2)$	0.156	0.102

Table 2: Bond lengths for compound (1) in (Å)

Parameters	Bond lengths	Parameters	Bond lengths
O1—C14	1.432	C4—C7	1.506
O2—C15	1.423	C5—C6	1.381
O2—C7	1.425	C8—C9	1.381
Cl1—C1	1.747	C8—C13	1.397
Cl2—C11	1.743	C8—C14	1.507
N1—C14	1.476	C9—C10	1.391
N1—C7	1.492	C10—C11	1.385
N1—C16	1.498	C11—C12	1.382
C1—C2	1.374	C12—C13	1.383
C1—C6	1.384	C15—C16	1.524
C2—C3	1.398	C16—C18	1.520
C3—C4	1.382	C16—C17	1.540

Spectroscopic analysis

The computed absorption wavelengths at TD-B3LYP/6-31G** level of theory have been tabulated in Table 5. Compound (1) showed four absorption peaks from 231 − 245 nm while compound (2) showed two absorption peaks at 214 nm and 245 nm. Moreover, no significant effect of solvent polarity on the absorption wavelengths and oscillator strengths is observed in studied compounds. The synthesis of compounds (1) and (2) are also witnessed in their NMR spectra. All the hydrogen atoms of the oxazolidine ring system were non-equivalent, and therefore, a separate signal was observed for each proton. The hydrogen atom flanked by the O- and N-atoms were most deshielded due to the inductive effect of two electron withdrawing groups and resonated in the range

Table 3: Bond lengths for compound (2) in (Å)

Parameters	Bond lengths	Parameters	Bond lengths
O3—C17	1.427	C11—C12	1.377
O3—C7	1.428	C11—H11	0.930
N1—C15	1.461	C12—C13	1.384
N1—C7	1.471	C12—H12	0.930
N1—C16	1.494	C13—H13	0.930
C1—C2	1.388	C14—H14A	0.960
C1—C20	1.389	C14—H14B	0.960
C1—H1	0.930	C14—H14C	0.960
C2—C3	1.376	C15—H15	0.983
C2—H2	0.930	C16—C18	1.514
C3—C4	1.379	C16—C17	1.520
C3—H3	0.930	C16—C19	1.520
C4—C5	1.390	C17—H17A	0.970
C4—H4	0.930	C17—H17B	0.970
C5—C20	1.397	C18—H18A	0.960
C5—C7	1.505	C18—H18B	0.960
C6—H6A	0.960	C18—H18C	0.960
C6—H6B	0.960	C19—H19A	0.970
C6—H6C	0.960	C19—H19B	0.970
C7—H7	0.988		

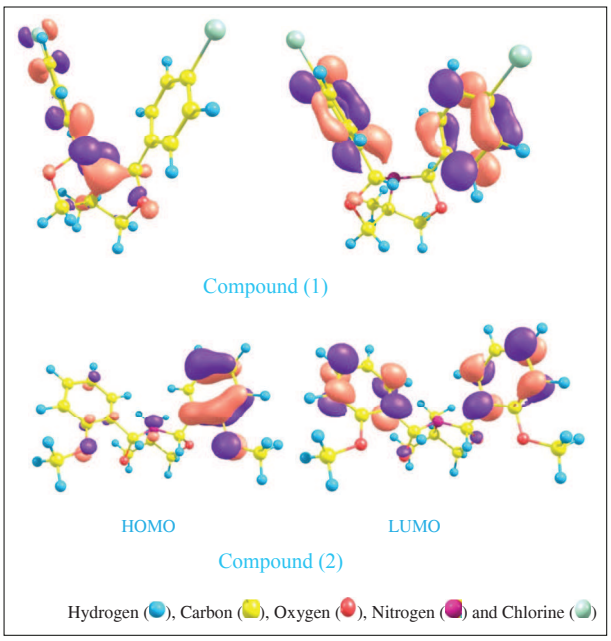

Figure 4: Representation of HOMOs and LUMOs density of studied compounds at B3LYP/6-31G** level of theory

Table 4: The experimental (Exp.) as well as ground states computed bond lengths (Å), bond angles (in degree) and torsion angles (in degree) at B3LYP/6-31G** level of theory

	Opt	Exp.	Opt	Exp.
	Compound (1)		Compound (2)	
	Bond lengths			
N1—C7	1.485	1.492	1.466	1.461
N1—C14	1.475	1.476	1.486	1.471
O1—C14	1.429	1.432	1.425	1.428
O1—C17	1.421	1.429	1.420	1.427
O2—C7	1.422	1.424	1.442	1.440
O2—C15	1.419	1.423	1.419	1.424
C4—C7	1.514	1.507	1.524	1.510
C8—C14	1.512	1.506	1.514	1.505
Cl1—C1	1.760	1.747	-	-
Cl2—C11	1.759	1.742	-	-
	Bond angles			
C7—N1—C14	117.36	117.40	114.11	114.77
C14—O1—C17	103.49	103.08	105.07	105.77
C7—O2—C15	105.26	103.88	104.98	104.36
	Torsion angles			
C4—C7—N1—C14	103.98	102.95	137.25	133.48
C4—C7—O2—C15	160.87	161.69	88.84	89.44
	Dipole moments			
	4.11	-	1.57	-

Table 5: The calculated HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}) and HOMO-LUMO energy gaps (E_{gap}) in eV of **1**[a] and **2**[b] at the B3LYP/6-31G**, absorption wavelengths (λ_a) (nm) and oscillator strengths (*f*) at TD-B3LYP/6-31G** level of theories in different solvents

Phase	Compound (1)		Compound (2)	
	f	λ_a	*f*	λ_b
Gas phase	0.1213	213	0.0502	214
	0.1083	221	0.0745	245
	0.0122	237		
	0.0032	245		
Acetone	0.0778	223	0.0629	215
	0.0179	238	0.0917	247
	0.0068	251		
Acetonitrile	0.0782	224	0.0607	215
	0.0176	238	0.0909	246
	0.0067	251		
DMF	0.0829	224	0.0710	215
	0.0186	238	0.0945	247
	0.007	251		
DMSO	0.0824	224	0.0697	215
	0.0184	238	0.0939	247
	0.007	251		
Methanol	0.0772	224	0.0580	215
	0.0174	238	0.0902	247
	0.007	251		

[a] E_{HOMO}, E_{LUMO} and E_{gap} are -6.44, -0.62 and 5.82 eV, respectively.
[b] E_{HOMO}, E_{LUMO} and E_{gap} are -5.78, -0.0003 and 5.78 eV, respectively.

of 5.6 to 5.0 ppm. The two protons in each methylene group are diastereotopic and appeared as doublets in the region from 4.1 to 3.6 ppm, a typical region for the protons of methylene units next to an oxygen atom. The aromatic protons in case of compound (1) resonated as four doublets each integrating to two protons, thus confirming the non-equivalence of two aromatic rings. However, two of the peaks were partially overlapping due to their comparable chemical shift values. In case of compound (2), the aromatic protons appeared as multiplets.

CONCLUSION

We report a facile synthetic route to synthesise two novel bicyclic oxazolidine compounds 3,5-bis(4-chlorophenyl)-7a-methyldihydro-1H-[1,3]oxazolo[3,4-c][1,3]oxazole (1) and 3,5-bis(2-methoxyphenyl)-7a-methyldihydro-1H-[1,3]oxazolo[3,4-c][1,3]oxazole (2). The condensation reaction between 2-amino-2-methyl-1,3-propandiol ($AmpdH_2$) and choloro- and methoxy-substituted aromatic aldehyde yielded bicyclic oxazolidines (1) and (2), respectively. These compounds were characterised using spectroscopic techniques as well as single crystal X-ray diffraction analysis. The B3LYP/6-31G** level of theory is a good choice to reproduce the experimental geometrical parameters. Intra-molecular charge transfer was observed in synthesised compounds. Moreover, no significant variation is observed on the absorption wavelengths by changing the solvent. The methoxy groups increased the energies of the highest occupied and unoccupied molecular orbitals.

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Supplementary material

CCDC 936163 contains the supplementary crystallographic data of compounds of this article. The data can be obtained free of charge *via http://www.ccdc.cam.ac.uk/conts/retrieving.html* or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ UK. Supplementary information associated with this article can be found in the online version.

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