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# Synthesis, Crystal Structures, Spectral Investigations, Conformational Analysis and DFT Studies of *N*- heterocyclic carbene precursors

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#### Abstract

Three new 2-hydroxyethyl substituted N-heterocyclic carbene (NHC) precursors were synthesized in this study. These NHC precursors were prepared from 1-(alkyl/aryl)benzimidazole and alkyl halides. Their structural characterizations were performed by elemental analysis, <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR and UV-Vis spectroscopy and single-crystal X-ray diffraction. The spectral features were also characterized by Density Functional Theory (DFT) at B3LYP/Lanl2dz//6-31G++(d,p) basis set. Two most stable conformers belonging to the compounds were found by potential energy surface (PES) scan, and the theoretical ground-state geometries were investigated. Among these conformers, the geometry of the conformer-I for all compounds matches almost well with the experimental results. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were calculated with GIAO approach and compared to the observed ones. Detailed vibrational assignments of the wavenumbers of the conformers were carried out based on the potential energy distribution (PED). Natural bond orbital (NBO) analysis was used to analyze the stability of the molecules arising from hyperconjugative interactions and charge delocalization. The HOMO-LUMO energy gap of the stable conformers was calculated for comparing their chemical reactivity behavior. Molecular electrostatic potential (MEP) diagrams were used to get information about the size, shape, charge density distribution and site of chemical reactivity of each stable conformer. The 3D Hirshfeld surfaces and the associated 2D fingerprint plots were also carried out to obtain an insight into the behavior of the interactions in the compounds.

Keywords: *N*-heterocyclic carbene, Crystal structure, Spectral investigations, Conformational analysis, DFT

# 1. Introduction

Carbene precursors such as benzimidazolium salts have attracted considerable interest in organic chemistry due to its structural and unique electronic properties, in recent years [1,2]. Particularly, these NHC precursors, which can form complexes almost with all of the transition metals [3-5], have shown strong activity in enzyme inhibition studies and have the focus of interest in their biological activity studies [6,7].

One approach used for the synthesis of benzimidazolium salts is the cyclization of ortho phenylenediamine with formic acid. Benzimidazolium salts are NHC precursors including two alkyl/aryl substituents that could be adjusted as steric bulk on two nitrogen atoms. A large number of different benzimidazolium salts have recently been described [8].

Our study on the single X-crystal structure of NHC precursors containing iodide ion has been published recently [9]. In this study, we investigated the structural and electronic properties of three new benzimidazolium salts by using single-crystal X-ray diffraction method and spectroscopic techniques <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR, and UV-Vis. In the literature, very few studies being important in terms of the biological activity and involving both experimental and theoretical details on the NHC precursors have been conducted [10]. So, to support the obtained experimental results with theoretical approaches, we performed comprehensive DFT studies. We aim to report the most important intramolecular interactions, to know the chemical reactivity behaviors of the compounds. Thus, frontier molecule orbitals (FMO), molecular electrostatic potential (MEP) and natural bond orbital (NBO) analyses were carried out. Additionally, to determine the most stable geometry of the compounds, a systematic quantum chemical study of the possible conformations, their relative stabilities were performed by using potential energy scan (PES) analysis. Vibrational modes of these stable conformers of the NHC salts were assigned based on the potential energy distribution (PED) analysis. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of the conformers were determined with gauge independent atomic orbital (GIAO) approach. To identify the intermolecular interactions, the 3D Hirshfeld surface analysis and the associated 2D fingerprint plots.

# 2. Experimental Section

Syntheses of the 2-hydroxyethyl substituted NHC precursors **1a-c** were prepared under an inert atmosphere in flame-dried glassware using standard Schlenk techniques. Iodoethanol, iodomethane, 2,4,6-trimethylbenzyl chloride, 2,4,5,6-tetramethylbenzyl chloride,

dimethylformamide, ethanol and diethyl ether as solvents and all other commercial chemicals were used without further purification. Melting points were identified in glass capillaries under air with an Electrothermal-9200 melting point apparatus. FT-IR spectra were saved in the range 400-4000 cm<sup>-1</sup> on Perkin Elmer Spectrum 100 FT-IR spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using a Bruker AS 400 spectrometer operating at 400 MHz (<sup>1</sup>H) and 100 MHz (<sup>13</sup>C). Chemical shifts ( $\delta$ ) are given in ppm relative to TMS, and coupling constants (*J*) in Hz. The UV spectrum was measured with the Shimadzu UV-1601 instrument. Elemental analyses were performed by İnönü University Scientific and Technological Research Center (Malatya, TURKEY).

# 2.1 Synthesis of bis(2-hydroxyethyl)benzimidazolium iodide, 1a

A mixture of 1-(2-hydroxyethyl)benzimidazole (162 mg, 10 mmol) and 2-hydroxyethyl iodide (172 mg, 10 mmol) was added in dry DMF (4 mL). The reaction mixture was stirred for 22 h at 70°C and 2 h at 110 °C temperatures. The excess of DMF was evaporated in vacuum. Diethyl ether was added to the reaction mixture and the white solid was filtered off. The crude product was crystallized in a mixture of ethyl alcohol-diethyl ether (1/3).Yield: 80 % (267 mg); m,p,: 219-221 °C;  $v_{(CN)}$ : 1561 cm<sup>-1</sup>;  $v_{(0-H)}$ : 3301 and 3400 cm<sup>-1</sup>. Anal. Calc. for C<sub>11</sub>H<sub>15</sub>IN<sub>2</sub>O<sub>2</sub>: C: 39.54; H: 4.52; N: 8.38. Found: C: 39.57; H: 4.49; N: 8.36. <sup>1</sup>H NMR (400 MHz, DMSO),  $\delta$  3.85 (s, 2H, -NCH<sub>2</sub>CH<sub>2</sub>OH); 4.60 (s, 2H, -NCH<sub>2</sub>CH<sub>2</sub>OH); 5.20 (s, 1H, -NCH<sub>2</sub>CH<sub>2</sub>OH); 7.69 and 8.09 (dd, m, 4H, *J*= 6.3, 3.1 Hz, Ar-*H*); 9.70 (s, 1H, 2-C*H*), <sup>13</sup>C NMR (400 MHz, DMSO),  $\delta$  50.0 (-NCH<sub>2</sub>CH<sub>2</sub>OH); 59.2 (-NCH<sub>2</sub>CH<sub>2</sub>OH); 114.4, 126.8 and 131.8 (Ar-*C*); 143.3 (2-*C*H).

# 2.2 Synthesis of 1-(2-hydroxyethyl)-3-(2,4,6-trimethylbenzyl)benzimidazolium iodide, 1b

According to the same procedure as salt **1a**, salt **1b** was prepared from 1-(2,4,6-trimethylbenzyl)benzimidazole (150 mg, 6 mmol) and 2-hydroxyethyl iodide (103 mg, 6 mmol). Yield: 79 % (200 mg), m,p,: 145-147 °C;  $v_{(CN)}$ : 1556 cm<sup>-1</sup>;  $v_{(O-H)}$ : 3324 cm<sup>-1</sup>. Anal. Calc. for C<sub>19</sub>H<sub>23</sub>IN<sub>2</sub>O: C: 54.04; H: 5.49; N: 6.63. Found: C: 54.00; H: 5.51; N: 6.65. <sup>1</sup>H NMR (400 MHz, DMSO),  $\delta$  2.26 and 2.30 (s, 9H, -NCH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>); 3.75 (dd, 2H, *J*= 9.8, 5.1 Hz, -NCH<sub>2</sub>CH<sub>2</sub>OH); 4.54 (t, 2H, *J*= 4.7 Hz, -NCH<sub>2</sub>CH<sub>2</sub>OH); 5.06 (t, 1H, *J*= 5.4 Hz, -NCH<sub>2</sub>CH<sub>2</sub>OH); 5.65 (s, 2H, -NCH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>); 7.04 (s, 2H, -NCH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>); 7.73 and 8.09 (m, dd, 4H, *J*= 8.7, 4.2 Hz, Ar-*H*); 9.06 (s, 2-C*H*),<sup>13</sup>C NMR (400 MHz, DMSO),  $\delta$  19.6 and 21.1 (-NCH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>); 45.6 (-NCH<sub>2</sub>CH<sub>2</sub>OH); 49.7 (-NCH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>); 58.9 (-NCH<sub>2</sub>CH<sub>2</sub>OH); 114.0, 114.4, 125.8, 127.2, 127.3, 130.0, 131.9, 132.0, 138.8 and 139.5 (Ar-*C*); 141.6 (2-*C*H).

2.3 Synthesis of 1-(2-hydroxyethyl)-3-(2,3,5,6-tetramethylbenzyl)benzimidazolium iodide, 1c

According to the same procedure as salt **1a**, salt **1c** was prepared from 1-(2,3,5,6-tetramethylbenzyl)benzimidazole (158 mg, 6 mmol) and 2-hydroxyethyl iodide (103 mg, 6 mmol). Yield: 72 % (188 mg), m,p,: 255-257 °C;  $v_{(CN)}$ : 1560 cm<sup>-1</sup>;  $v_{(O-H)}$ : 3287 cm<sup>-1</sup>. Anal. Calc. for C<sub>20</sub>H<sub>25</sub>IN<sub>2</sub>O: C: 55.05; H: 5.78; N: 6.42. Found: C: 55.01; H: 5.80; N: 6.39. <sup>1</sup>H NMR (400 MHz, DMSO),  $\delta$  2.17 and 2.26 (s, 12H, -NCH<sub>2</sub>C<sub>6</sub>H(CH<sub>3</sub>)<sub>4</sub>); 3.76 (s, 4H, -NCH<sub>2</sub>CH<sub>2</sub>OH); 4.54 (s, 4H, -NCH<sub>2</sub>CH<sub>2</sub>OH); 5.04 (s, 1H, -NCH<sub>2</sub>CH<sub>2</sub>OH); 5.72 (s, 2H, -NCH<sub>2</sub>C<sub>6</sub>H(CH<sub>3</sub>)<sub>4</sub>); 9.00 (2-CH); 7.16 (s, 1H, -NCH<sub>2</sub>C<sub>6</sub>H(CH<sub>3</sub>)<sub>4</sub>); 7.74 and 8.13 (m, dd, *J*= 20.9, 7.4 Hz, 4H, Ar-H), <sup>13</sup>C NMR (400 MHz, DMSO),  $\delta$  15.8 and 20.6 (-NCH<sub>2</sub>C<sub>6</sub>H(CH<sub>3</sub>)<sub>4</sub>); 46.3 (-NCH<sub>2</sub>CH<sub>2</sub>OH); 49.8 (-NCH<sub>2</sub>C<sub>6</sub>H(CH<sub>3</sub>)<sub>4</sub>); 59.0 (-NCH<sub>2</sub>CH<sub>2</sub>OH); 114.2, 114.6, 127.0, 127.1, 128.6, 132.0, 132.1, 133.4, 134.7 and 134.9 (Ar-C); 141.9 (2-CH).



Scheme 2. Synthesis of 1-(2-hydroxyethyl)benzimidazolium salts 1a-c

b

С

2.4 Single-crystal X-ray diffraction

a

Single-crystal X-ray data of the compounds **1a-c** were recorded at room temperature by  $\omega$ scan technique, on a Rigaku-Oxford Xcalibur diffractometer with an EOS-CCD area detector operated at 50 kV and 40 mA using graphite-monochromated MoK $\alpha$  radiation ( $\lambda$ = 0.71073 Å) from an enhance X-ray source with CrysAlis<sup>*Pro*</sup> software [11]. Data reduction and analytical absorption corrections were performed by CrysAlis<sup>*Pro*</sup> program [12]. The structural solution, refinement, and analysis were performed using OLEX2 [13]. The crystal structure of the compounds was solved using *Intrinsic Phasing* method with SHELXT and refined by full-matrix least-squares on *F*<sup>2</sup> in SHELXL [14,15]. Anisotropic thermal parameters were applied to all nonhydrogen atoms. Except for the O–H hydrogen atoms in the compound **1a**, all other hydrogen atoms were placed using standard geometric models and with their thermal parameters riding on those of their parent atoms (O–H = 0.82 Å; C–H = 0.93, 0.96 and 0.97 Å). In both hydroxyethyl groups in **1a**, O–H hydrogen atoms were located in difference Fourier map and freely isotropically refined. DFIX 0.86 Å was also applied to fix the O1–H1 distance. To ensure satisfactory refinement of disordered hydroxyethyl group in the structure, rigid-bond restraint RIGU and isotropic restraint ISOR were applied to the hydroxyethyl group of the compound **1b**.

	1a	1b	1c
Empirical Formula	$C_{11}H_{15}N_2O_2I$	$C_{19}H_{23}N_2OI$	$C_{20}H_{25}N_2OI$
Formula weight	334.15	422.29	436.32
Temperature/K	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group, Z	$P2_{1}/n, 4$	$P2_{1}/c, 4$	<i>P2</i> <sub>1</sub> / <i>c</i> , 4
a/Å	8.9682(5)	8.7386(4)	9.7610(6)
<i>b</i> /Å	10.6343(4)	15.4147(8)	13.1166(9)
c/Å	13.8686(6)	14.0661(6)	15.7840(9)
$\beta/^{\circ}$	93.754(4)	93.971(4)	102.110(6)
Volume/Å <sup>3</sup>	1319.82(11)	1890.20(15)	1975.9(2)
$\rho_{calc}g/cm^3$	1.682	1.484	1.467
$\mu/mm^{-1}$	2.416	1.700	1.629
<i>F</i> (000)	656	848	880
Crystal size/mm <sup>3</sup>	$0.488 \times 0.380 \times 0.205$	$0.428 \times 0.348 \times 0.207$	$0.399 \times 0.275 \times 0.192$
Reflections collected	4669	5903	6355
Independent reflections	2498 [ $R_{int} = 0.021$ ]	3560 $[R_{int} = 0.021]$	$3710 [R_{int} = 0.023]$
Parameters	153	212	222

Table 1. Crystallographic data and structure refinement for the compounds 1a-c.

	Journal Pre-proof											
Goodness-of-fit on $F^2$	1.038	1.040	0.987									
$R, wR_2[I > 2\sigma(I)]$	$R_1 = 0.0312, wR_2 = 0.0622$	$R_1 = 0.0526, wR_2 = 0.1265$	$R_1 = 0.0447, wR_2 = 0.0966$									
$R$ , $wR_2$ (all data)	$R_1 = 0.0449, wR_2 = 0.0689$	$R_1 = 0.0709, wR_2 = 0.1384$	$R_1 = 0.0808, wR_2 = 0.1170$									

# 2.5 Theoretical Studies

The quantum chemical calculations have been performed at DFT (B3LYP) methods with Lanl2dz//6-31G++(d,p) basis set using Gauss–View6 molecular visualization and Gaussian 09W program packages [16,17]. In order to determine the most stable conformers of the molecular structures, the conformational analysis in the gas phase was carried out. Two stable structures were found for each compound by PES (potential energy surface) scan. The vibrational frequency calculations were performed at the same level of the theory, and the fundamental normal modes of all the conformers were assigned based on the potential energy distribution (PED). The <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of each conformer of the **1a-c** were obtained by using the gauge invariant atomic orbital (GIAO) method in the gaseous phase [18]. Values for the <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced to TMS. The natural bonding orbital (NBO) calculations were performed using NBO 3.1 program as implemented in Gaussian 09W package to get detailed insight about the intramolecular interactions and investigate charge transfer, delocalization or hyperconjugative interactions in the molecular systems of **1a-c** [19]. Frontier molecular orbitals (FMO) and molecular electrostatic potential (MEP) surfaces were also generated to understand the chemical reactivity tendencies. Molecular Hirshfeld surfaces are generated by CrystalExplorer version 17.5 computer program [20].

### 3. Results and Discussions

# 3.1 Structural Determination of 1a-c

The molecular view of the compounds **1a-c** is represented in Figs. 1, 2 and 3. All compounds crystallize in the monoclinic crystal system. Each unit of the salts consists of a benzimidazolium cation and an iodide anion. In the asymmetric unit of the **1a**, the NHC cation contains two hydroxyethyl groups, which are arranged into U–shaped, extend parallel to the *a*-axis. The twist angles of hydroxyethyl around the benzimidazole ring system are very similar [N1–C8–C9–O1 =  $65.3(4)^\circ$ , N2–C10–C11–O2 =  $-66.4(4)^\circ$ ]. In **1b** and **1c**, NHC ligands connect to trimethylbenzyl and tetramethylbenzyl fragments, respectively, besides the hydroxyethyl groups. N-benzimidazole ring systems are almost coplanar with a mean deviation of 0.009 Å for **1a**, 0.010

Å for **1b** and 0.019 Å for **1c**. Bond parameters such as bond lengths, bond angles, and torsion angles are comparable with similar compounds in our previous study and related studies in the literature [9, 21-23]. In the crystal structure of the **1a**, the cation molecule connects to iodide anion by hydroxyethyl groups (Table 2). Also, there is a C–H···O type intermolecular weak interaction, forming  $R_2^2(12) R_6^4(20)$  dimer graph-set motif together with the hydrogen bonds, is responsible for the stabilization of the structure (Fig. 1b-c). In the crystal structure of **1b** and **1c**, there is only a hydrogen bonding interaction which occurs between the hydroxyethyl oxygen atom of the cation molecule and iodide anion [21, 24]. For both compounds, the iodide anions play role on the stabilization of the crystal structures. The crystal packing views are illustrated in Fig. 2b and 3b.



**Fig. 1.** Single crystal X-ray structure of **1a** showing (**a**) Ellipsoid plot (30% probability level) (**b**)  $R_2^2(12) R_6^4(20)$  dimeric motif through the O–H···I hydrogen bonds and C–H···O intermolecular interactions (**c**) 1D ladder-like motif of the iodide anions along the *b* axis. All hydrogen atoms except those participating in the interactions were omitted for clarity.



**Fig. 2.** Single crystal X-ray structure of **1b** showing (**a**) Ellipsoid plot (30% probability level) (**b**) Packing of the crystal structure viewed along the *c*-axis.



**Fig. 3.** Single crystal X-ray structure of **1c** showing (**a**) Ellipsoid plot (30% probability level) (**b**) Packing of the crystal structure viewed along the *c*-axis.

Compound	D-H···A	D-H	Н…А	D····A	D-H···A
1a	01–H1…I1	0.85	2.77	3.594(4)	165
	O2–H2…I1	0.85	2.60	3.427(3)	165
	C1–H1A····O2 <sup>i</sup>	0.93	2.16	3.046(4)	160
1b	O1–H1…I1	0.82	2.57	3.383(8)	170
1c	O1–H1A…I1	0.82	2.60	3.423(4)	176

**Table 2.** Hydrogen-bonding and weak intermolecular interactions [Å,°] for the title compounds.

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

#### 3.2 Molecular Geometry and Conformational Analysis

Optimized structural parameters of three NHC salts were calculated in the gaseous phase via density functional theory [DFT/B3LYP/LanL2DZ//6-31G++(d,p)]. In order to find the conformational stabilities of the NHC complexes, 1D relaxed potential energy surface (PES) scans were performed around torsion angles  $(\tau)$  of two sides of the benzimidazole fragments C10–C11–C16) and  $\tau_6$ (N2–C10–C11–C12)]. On account of the same torsion angle, we selected only  $\tau_2(N1-C8-C9-O1)$  for the conformational analysis in here. Investigation results for the other stable conformers were given in the supplementary information file. Scanning was started from 60° to 280° by taking 4° intervals (i.e., 50 steps) and a total of 51 scan steps. Fig. 4 indicates the potential energy surface curve of the NHC salt 1a, while the other stable conformers are in supplementary data (Fig. S1 and S2). The values reveal that global minimum structures are the most stable conformers, and they match well with the experimental one. The selected geometric parameters such as bond distances, bond angles and torsion angles of the two most stable conformers for the selected scan coordinate angle  $\tau_2(N1-C8-C9-O1)$  of the **1a-c** were computed and compared with the experimental X-ray data in Table 3. It is clear from the table, the calculated bond lengths are slightly higher than the experimental ones, which is well known that the experimental molecular structure was in solid-state form, while the theoretical computations of the isolated structure were carried out in the gaseous phase of the molecule. The calculated total energies and the energy differences between the most stable two conformers Conf-I and Conf-II for the structures are listed in Table 4. Given that its energy is lower than Conf-II, Conf-I is the most stable conformer for the selected scan coordinate angle  $\tau_2(N1-C8-C9-O1)$ .

		<b>1</b> a			1b			1c	
	Exp.	ConfI	ConfII	Exp.	ConfI	ConfII	Exp.	ConfI	ConfII
Bond Lengths									
O1–C9	1.408(5)	1.442	1.440	1.311(3)	1.444	1.438	1.424(7)	1.444	1.446
O2–C11	1.417(4)	1.442	1.446	-	-	-	-	-	-
N1–C8	1.474(4)	1.478	1.478	1.463(6)	1.477	1.479	1.468(6)	1.477	1.474
N2-C10	1.472(4)	1.478	1.481	1.475(6)	1.488	1.496	1.478(6)	1.487	1.487
C8–C9	1.510(5)	1.530	1.550	1.518(8)	1.532	1.546	1.495(8)	1.532	1.534
C10-C11	1.512(5)	1.530	1.530	1.509(7)	1.518	1.511	1.513(6)	1.522	1.520
Bond Angles									
01C9C8	111.6(3)	107.96	109.47	106.1(6)	109.03	108.95	107.3(5)	108.97	114.11
O2-C11-C10	110.9(3)	107.97	108.44	-	0	-	-	-	-
C1-N1-C8	125.3(3)	124.71	123.82	124.9(4)	124.70	124.27	125.3(4)	124.67	124.78
C1-N2-C10	125.2(3)	124.71	125.02	127.2(4)	124.31	126.21	128.0(4)	124.56	124.54
N1-C8-C9	111.6(3)	111.89	112.13	109.5(4)	112.21	112.21	110.7(4)	112.10	114.05
N2-C10-C11	111.8(3)	111.91	112.30	112.6(4)	113.04	113.46	111.1(4)	112.85	113.29
<b>Torsion Angles</b>									
C1-N1-C8-C9	-86.7(4)	-62.44	-105.89	-82.6(6)	-58.29	-96.34	79.0(6)	59.10	-40.44
N1-C8-C9-O1	65.3(4)	64.00	-152.00	63.4(9)	65.02	161.02	-63.8(6)	-64.56	56.20
C1-N2-C10-C11	92.6(4)	62.38	43.05	-5.0(9)	-51.49	-26.80	-9.3(7)	46.46	46.80
N2-C10-C11-O2	-66.4(4)	-63.99	69.39	-	-	-	-	-	-
N2-C10-C11-C12	-	-	-	83.7(6)	116.26	99.17	-81.6(5)	-119.03	-114.02
N2-C10-C11-C16	-	-	-	-98.4(6)	-65.37	-81.56	97.2(5)	62.02	66.94

**Table 3.** The selected geometric parameters of two conformers (for the scan coordinate angle N1–C8–C9–O1) of each compound.



Fig. 4. Representation of potential energy surface (PES) scan of the compound 1a with torsion angles  $\tau_{1.4}$ 

# 3.3 Global reactivity descriptors, FMO (frontier molecular orbital) analysis, MEP (molecular electrostatic potential)

Frontier Molecular Orbital (FMO) analysis provides important information about the electronic properties and molecular reactivity of a compound. The highest occupied molecular orbital (HOMO), as an electron donor, represents the distribution and energy of the least tightly held electrons in the molecule, while the lowest unoccupied molecular orbital (LUMO) as an electron acceptor, shows the ability to obtain an electron. The HOMO-LUMO analysis is used to explain the charge transfer within a molecule. If in a molecule, HOMO is not doubly occupied or the molecules do not have a large HOMO-LUMO energy gap, it is chemically reactive. The higher energy values of HOMO, the more tendency to donate electrons to an appropriate acceptor. Similarly, the lower values of LUMO energy show more probability to accept electrons. In fact, the energy of the HOMO is a good approximation to the lowest ionization potential of the molecule but the energy of the LUMO generally is a poor approximation to the molecule's electron affinity [25]. Molecular electrostatic potential (MEP) is related to the electronic density and is a very useful descriptor to predict the possible reactive sites for electrophilic and nucleophilic attack reactions as well as hydrogen bonding interactions [26,27]. In the present study, in order to investigate the chemical reactivity of these three NHC salts, the frontier molecular orbital energies were calculated at DFT/B3LYP/LanL2DZ//6-31G++(d,p) level for

each stable conformer of selected torsion angle  $\tau_2$ . Table 5 displays some quantum chemical quantities belonging these conformers such as electronegativity ( $\chi$ ), chemical hardness ( $\eta$ ), softness(*S*), chemical potential ( $\mu$ ), charge transfer capability ( $\Delta N_{max}$ ) and electrophilicity index ( $\omega$ ). In addition to the ionization energy (*I*) [28] and electron affinity (*A*) [29] provided by the Koopmans Theorem [30], these quantum chemical identifiers proposed by Parr and co-worker [31,32] also provide theoretical insights into the chemical reactivity of a molecule. According to the table, it can be said that Conf-II of **1b** is the soft conformer with the lowest hardness value, the best electrophile with the biggest electrophilicity index and has the most charge transfer capability. Table 6 shows the HOMO-LUMO amplitudes and MEP diagrams of the stable conformers. For all structures, HOMO for the Conf-I is localized on the iodide anion, whereas LUMO is expanded on the benzimidazole moiety of the cation molecules.

MEP diagrams of the complexes reveal that the iodide anion center of the Conf-II of **1b** has the red color which means this region is the electron-rich region of the compound and therefore the nucleophilic attack center of this molecule. NBO analysis also proves this result. The iodide atom of Conf-II of **1b** has the most maximum negative charge value [-0.85973] comparing to all other molecules, which may due to the unfavorable geometry of Conf-II. Also, the resonance energy of the electronic transition from LP(1)I1 to the O1-H1 has the lowest E(2) energy (see Table 7). Therefore, the lone pair electrons of the iodide anion do not have as much delocalization energy as the iodide atoms of other conformers and this makes this region is the electron-rich region.

Torsion angle			
Compound 1a	Total Energ	gy (kcal/mol)	ΔE (kcal/mol)
	Conf –I	Conf–II	
$\tau_1(C1-N1-C8-C9)$	-438850.5613	-438847.6183	2.94
$\tau_2(N1-C8-C9-O1)$	-438850.5613	-438845.7775	4.78
$\tau_3(N2-C10-C11-O2)$	-438850.5613	-438850.1828	0.38
$\tau_4(C1-N2-C10-C11)$	-438850.5613	-438845.5465	5.01
Compound 1b			
$\tau_1(C1-N1-C8-C9)$	-585953.3426	-585953.4168	-0.17
$\tau_2(N1-C8-C9-O1)$	-585953.3426	-585949.0091	4.33
$\tau_5(N2-C10-C11-C16)$	-585953.3426	-585952.6999	0.64
$\tau_6(N2-C10-C11-C12)$	-585953.3426	-585952.6973	0.64
Compound 1c			
$\tau_1(C1-N1-C8-C9)$	-610614.7007	-610610.7694	3.93
$\tau_2(N1-C8-C9-O1)$	-610615.6848	-610615.1329	0.44
$\tau_5(N2-C10-C11-C16)$	-610611.8593	-610614.9651	-3.11
τ <sub>6</sub> (N2–C10–C11–C12)	-610611.7914	-610614.973	-3.18

**Table 4.** Theoretically computed relative energies and the energy differences between the most stable two conformers Conf-I and Conf-II for structures **1a-c.**

**Table 5.** The calculated quantum chemical parameters (eV) for each conformer (for the scan coordinate angle N1–C8–C9–O1) of NHC salts **1a-c.** 

	1:	a	1	b	1c		
	Conf-I	Conf-II	Conf-I	Conf-II	Conf-I	Conf-II	
HOMO (- <i>I</i> )	-4.79	-5.03	-4.69	-4.56	-4.64	-4.80	
LUMO (-A)	-2.09	-2.15	-1.79	-2.12	-1.78	-1.63	
$\mathbf{E_{gap}}$	2.7	2.88	2.9	2.44	2.86	3.17	
χ	3.44	3.59	3.24	3.34	3.21	3.22	
η	1.35	1.44	1.45	1.22	1.43	1.59	
μ	-3.44	-3.59	-3.24	-3.34	-3.21	-3.22	
ω	4.38	4.48	3.62	4.57	3.60	3.27	
S	0.37	0.35	0.35	0.41	0.35	0.31	
$\Delta N_{max}$	2.55	2.49	2.23	2.74	2.24	2.03	

1a			
	НОМО	LUMO	MEP
Conf-I			
Conf-II			
LD Conf-I			V
			C C C C C C C C C C C C C C C C C C C
lc Conf I			
C0111-1			

**Table 6.** HOMO and LUMO amplitudes (isovalue:0.02) and MEP diagrams (isovalue:0.0004) of each stableconformers (for the scan coordinate angle N1–C8–C9–O1) for the compounds at B3LYP/Lanl2dz//6-31G++(d,p).

Conf-II		

# 3.4 Natural Bond Orbital (NBO) Analysis

The natural bond orbital (NBO) calculations provide an efficient method in order to understand the intramolecular interactions between the bonds and the charge transfer within the molecular systems. In the present work, the second-order perturbation theory analysis of Fockmatrix for the stable conformers of the structures 1a-c was carried out to evaluate the donoracceptor interactions on the NBO basis. The larger the E(2) value, the more intense is the interaction between electron donors and acceptors, i.e. more donating tendency from electron donors to electron acceptors and greater the extent of conjugation of the whole system [33]. Table 7 indicates the stabilization energy, orbitals' occupancies and Fock matrix element for the conformers of selected torsion angle  $\tau_2$ (N1-C8-C9-O1) for three NHC salts. As it is expected, the strongest donations occur in the aromatic rings, especially in the benzimidazolium ring for all structures, which give rise to the stabilization of the molecules. The stabilization energy for LP(1) N1 $\rightarrow \pi^*(N2-C1)$  charge transfer for all conformers is similar to each other and calculated in the range of 79.49–86.62 kJ/mol. In the structure 1b, the Conf-II, the donation from the antibonding orbital of  $\pi^*(C11-C12)$  to the  $\pi^*(C13-C14)$  has the strongest energy of 232.50 kJ/mol. The important second-order perturbative energies belonging to the stable conformers of the torsion angles  $\tau_{1,3,4}$  are tabulated in supporting information file (Table S1).

**Table 7.** The Second Order Perturbation Theory Analysis Results of the Fock Matrix in NBO Basis for the stable conformers of selected torsion angle  $\tau_2(N1-C8-C9-O1)$  at B3LYP/Lanl2dz//6-31G++(d,p) level of the theory. The greatest three stabilization energy is shown.

	Donor(i)	Acceptor(j)	ED <sub>i</sub> (e)	ED <sub>j</sub> (e)	E(2) kJ/mol	$E_j-E_i(a.u)$	F <sub>i,j</sub> (a.u)						
	Compound 1a												
Conf-I													
	π* C2–C7	π* C3–C4	0.47354	0.30052	141.84	0.02	0.081						
	π* С2−С7	π* C5–C6	0.47354	0.30051	141.82	0.02	0.081						
	LP(1) N1	π* N2–C1	1.52488	0.49419	84.07	0.21	0.120						

	Journal Pre-proof												
	LP(1) I1	σ* O1–H1	1.99928	0.07044	0.64	0.89	0.022						
Conf-II													
	π* C2–C7	π* С3−С4	0.47709	0.30238	133.24	0.02	0.081						
	π* C2–C7	π* C5–C6	0.47709	0.30729	144.06	0.02	0.081						
	LP(1) N1	π* N2–C1	1.52127	0.50757	85.82	0.21	0.121						
	LP(1) I1	σ* 01–H1	1.99689	0.02600	0.43	0.92	0.018						
			Compour	nd 1b									
Conf-I													
	π* C2–C7	π* С3−С4	0.47375	0.30978	160.64	0.02	0.081						
	π* C2–C7	π* С5–С6	0.47375	0.30622	150.76	0.02	0.081						
	LP(1) N1	π* N2–C1	1.53659	0.50806	81.17	0.21	0.119						
	LP(1) I1	σ* O1–H1	1.99891	0.07015	0.69	0.90	0.023						
Conf-II													
	π*C11–C12	π*C13–C14	0.38724	0.32525	232.50	0.01	0.082						
	π* C2–C7	π* С3–С4	0.47707	0.29925	136.96	0.02	0.081						
	π* C2–C7	π* C5–C6	0.47707	0.30590	150.66	0.02	0.080						
	LP(1) N1	π* N2–C1	1.51560	0.49369	86.25	0.21	0.120						
	LP(1) I1	σ* 01–H1	1.99873	0.03471	0.33	0.92	0.016						
			Compou	nd 1c									
Conf-I													
	π* С2−С7	π* С3−С4	0.47318	0.30904	163.55	0.02	0.081						
	π* C2–C7	π* C5–C6	0.47318	0.30619	153.73	0.02	0.081						
	LP(1) N2	π* N1–C1	1.52008	0.51898	86.62	0.21	0.121						
	LP(1) I1	σ* O1–H1	1.99895	0.07257	0.70	0.89	0.023						
Conf-II													
	π* C2–C7	π* C3–C4	0.47386	0.31707	172.10	0.02	0.081						
	π* C2–C7	π* C5–C6	0.47386	0.31892	176.36	0.02	0.081						
	LP(1) N1	π* N2–C1	1.54688	0.51776	79.49	0.21	0.118						
	LP(1) I1	σ* 01–H1	1.99895	0.05469	0.44	0.91	0.018						

# 3.5 Vibrational Analysis

The FT-IR spectra of the 2-hydroxyethyl substituted NHC precursors **1a-c** were compared with the corresponding simulated ones. The vibrational spectral assignments of the stable conformers were carried out with the help of potential energy distribution (PED) analysis. The PED contributions corresponding to each of the observed frequencies are listed in Table 8. Also, the recorded and calculated FT-IR spectra of the NHC salts can be seen from Fig. S3-S4 (suppl. data).

When the FT-IR spectra were investigated, the bands were observed in the range 3024-3146 cm<sup>-1</sup> in the high-frequency region correspond to C-H stretching vibrations of the aromatic rings. These vibration modes were calculated in the range of 3226-3246 cm<sup>-1</sup> for three stable conformers. The band at 1064, 1083 and 1073 cm<sup>-1</sup> corresponds to the symmetric C-O stretching for **1a-c**, respectively. The corresponding modes for the stable conformers were assigned at 1056-1060 cm<sup>-1</sup> for **1a**, 1090-1065 cm<sup>-1</sup> for **1b**, 1073-1078 cm<sup>-1</sup> for **1c**. The O-H stretching on the hydroxyethyl groups was observed at 3301-3400, 3324 and 3287 cm<sup>-1</sup> for **1a-c**, respectively. We calculated them in the range of 3267-3511 cm<sup>-1</sup>. The FT-IR data clearly indicated the presence of the C-N stretching at 1561, 1556 and 1560 cm<sup>-1</sup> for **1a-c**, respectively. Theoretically, they were found very close to the experimental values [1573-1575 cm<sup>-1</sup> for the conformations of **1a**, 1571-1568 cm<sup>-1</sup> for **1b** and 1577-1575 cm<sup>-1</sup> for **1c**. It is worth noting that the vibration modes assignments of the three conformers have differed at somewhere depending on the conformational structure.

**Table 8.** The selected vibrational assignments (in cm<sup>-1</sup>) of the stable conformers of selected torsion angle  $\tau_2$ (N1-C8-C9-O1) of 1a-c, with the percentage of potential energy distribution.

1a - C	Calculate	ed wavenumbe	r (unscale	ed)	1b - C	Calculate	d wavenum	ber (unsc	aled)	1c - Calculated wavenumber (unscaled				caled)
Exp.	ConfI	PED(%)	ConfII	PED(%)	Exp.	ConfI	PED(%)	ConfII	PED(%)	Exp.	ConfI	PED(%)	ConfII	PED(%)
3362	3355	$vC_{1}(65)$	3332	$vC_{l}(17)$	3352	3366	$vC_{1}(64)$	3153	$vC_{l}(24)$	3284	3366	$vC_{l}(65)$	3344	$vC_{1}(16)$
3301	3288	$vO_1(18)$	3511	$vO_{l}(32)$	3324	3280	$vO_1(32)$	3437	$vO_1(33)$	3287	3267	$vO_{1}(32)$	3344	$vO_{1}(16)$
3400	3288	$vO_2(18)$	3333	vO <sub>2</sub> (16)										
3131	3246	$v_s C_6 + C_3(21)$	3246	$v_s C_3(28)$	3131	3246	$v_s C_3(28)$	3245	$v_s C_3(26)$	3146	3246	$v_s C_3(13)$	3244	$v_s C_3(25)$
		$v_s C_5 + C_4(21)$		$+C_4(22)$			$+C_4(22)$		$+C_4(21)$			$+C_4(15)$		$+C_4(20)$
				$+C_{5}(17)$			$+C_{5}(17)$		$+C_{5}(18)$			$+C_{5}(21)$		$+C_{5}(18)$
				+C <sub>6</sub> (15)			$+C_6(15)$		$+C_6(18)$			$+C_{6}(33)$		$+C_{6}(20)$
3024	3228	$v_a C_6 + C_3(19)$	3228	$v_a C_3(17)$	3082	3227	$v_a C_3(23)$	3227	$v_a C_3(18)$	3089	3226	$v_a C_3(23)$	3225	$v_a C_3(18)$
		$v_a C_5 + C_4(20)$		$+C_4(18)$			$+C_4(23)$		$+C_4(19)$			$+C_4(23)$		$+C_4(20)$
				$+C_{5}(22)$			$+C_{5}(18)$		$+C_5(21)$			$+C_{5}(17)$		$+C_{5}(21)$
				$+C_{6}(22)$			$+C_6(15)$		$+C_{6}(21)$			$+C_6(15)$		$+C_{6}(20)$
2956	3157	$v_a C_8 + C_{10}(19)$	3172	$v_a C_8(17)$	2968	3151	$v_a C_8(26)$	3165	$v_a C_8(15)$	2937	3152	$v_a C_8(25)$	3121	$v_a C_8(14)$
			3149	$v_a C_{10}(29)$		3136	$v_a C_{10}(14)$	3143	$v_a C_{10}(20)$		3147	$v_a C_{10}(13)$	3160	$v_a C_{10}(24)$
			3130	$v_a C_9(18)$							3110	$v_a C_9(15)$	3121	$v_a C_9(13)$
			3100	$v_a C_{11}(16)$										
-	-	_	_	-	3190	3192	$vC_{12}(55)$	3204	vC14(61)	3021	3185	$vC_{14}(60)$	3184	$vC_{14}(60)$
						3185	$vC_{15}(54)$	3190	$vC_{17}(61)$			14()		14()
-	-	-	-	-	2958	3121	$v_a C_{10}(16)$	3118	$v_a C_{10}(13)$	2915	3128	$v_a C_{20}(16)$	3128	$v_a C_{20}(19)$
						3116	$v_a C_{18}(30)$	3119	$v_a C_{18}(25)$		3114	$v_a C_{19}(23)$	3107	$v_a C_{19}(21)$
						3120	$v_a C_{17}(22)$	3111	$v_a C_{17}(21)$		3108	$v_a C_{18}(22)$	3114	$v_a C_{18}(22)$

						Journ	al Pre-pr	oof						
											3108	$v_a C_{17}(23)$	3128	$v_a C_{17}(16)$
-	-	-	-	-	2907	3041	$v_s C_{17}(25)$	3031	$v_s C_{17}(25)$	2873	3034	$v_s C_{17}(21)$	3030	$v_s C_{17}(17)$
						3039	$v_s C_{18}(25)$	3043	$v_s C_{18}(28)$		3033	$v_s C_{18}(21)$	3042	$v_s C_{18}(27)$
						3035	$v_s C_{19}(19)$	3034	$v_s C_{19}(17)$		3042	$v_s C_{19}(27)$	3032	$v_s C_{19}(25)$
											3032	$v_s C_{20}(17)$	3037	$v_s C_{20}(24)$
1561	1573	$vC_1N(3)$	1575	$vC_1N(3)$	1556	1571	$vC_lN(2)$	1568	$vC_lN(2)$	1560	1577	$v_1 N(2)$	1575	$vC_1N(2)$
1064	1056	vCO(2)	1060	vCO(2)	1083	1090	vCO(1)	1065	vCO(1)	1073	1073	vCO(3)	1078	vCO(3)
1013	1027	opb	1028	opb	1015	1023	opb	1028	opb	1033	1023	opb	1020	opb
		$C_4HC_5H$		$C_4HC_5H$			$C_4HC_5H$		$C_4HC_5H$			$C_4HC_5H$		$C_4HC_5H$
		(14)		(14)			(14)		(12)			(14)		(14)

# 3.6<sup>13</sup>C and <sup>1</sup>H NMR studies

The data of the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra obtained for 2-hydroxyethyl substituted NHC precursors **1a-c** in DMSO- $d_6$  are given in the experimental section. The plots of spectra are given in supporting data (Fig. S5-7). The theoretical GIAO <sup>1</sup>H and <sup>13</sup>C chemical shift calculations (with respect to TMS) were carried out using the DFT/B3LYP/6-31G++(d,p) basis set and compared with experimental ones. The results of the calculations regarding the conformations of torsion angle  $\tau_2(N1-C8-C9-O1)$ , which is common to all compounds, are listed in supporting data (Table S4) together with the experimental values. The <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are converted to the TMS scale by subtracting the calculated absolute chemical shielding of TMS ( $\delta = \Sigma_0 - \Sigma$ ) where  $\delta$  is the chemical shift,  $\Sigma$  is the absolute shielding and  $\Sigma_0$  is the absolute shielding of TMS, whose values are 32.33 and 194.58 ppm for B3LYP/6-31G++(d,p), respectively. When the NMR spectra were examined, the -CH<sub>2</sub> protons of hydroxyethyl group of the NHC precursors (1a and 1c) appeared downfield shifted singled at 3.85-4.60 and 3.76-4.54 ppm for **1a** and **1c**, respectively. However, the -CH<sub>2</sub> protons of hydroxyethyl group of the NHC precursor 1b appeared downfield shifted double-doubled at 3.75 and tripled at 4.54 ppm. These signals were calculated for the conformers as 3.56-4.20 and 3.80-4.27 ppm for 1a, 3.34-3.57 and 3.39-5.35 ppm for 1b, 3.30-4.34 and 3.23-4.64 ppm for 1c.

The carbon resonances of the NHC precursors (**1a-c**) for hydroxyethyl group in the <sup>13</sup>C NMR spectrum appeared downfield at 50.0-59.2, 45.6-58.9 and 46.3-59.0 ppm for **1a-c**, respectively. As expected, the chemical shifts of the Conf-I of all the compounds are more consistent with these values, which are 49.62-57.64, 49.26-58.47 and 49.19-58.11 ppm, respectively. The characteristic proton peak on the hydroxyl groups (-OH) of the NHC precursors **1a-c** appeared highly downfield shifted singled at 5.20, 5.06 and 5.04 ppm for **1a-c**, respectively. These signals were found quite low [in the range of 2.49-3.62 ppm] theoretically. The NCHN carbon resonances of the

compounds in the <sup>13</sup>C NMR spectrum appeared highly downfield at 143.3, 141.6 and 141.9 ppm, respectively. We found these signals for the conformers I-II at 139.97-136.67 ppm, 136.95-136.04 ppm, 137.52-138.27 ppm, for **1a**-c, respectively.

# 3.7 UV-Vis spectral analysis

When the 2-hydroxyethyl substituted NHC precursors **1a-c** were dissolved in chloroform at 25 °C and, the UV-Vis spectra of them, which were depicted in Fig. 5, were observed in the range of 200–500 nm. The UV-Vis spectra of the NHC precursors **1a-c** were observed as three absorption bands from 210 to 270 nm in the CHCl<sub>3</sub>. The iodides in all NHC precursors **1a-c** have peak absorbances at 210 nm.[11] That the absorption bands were at 230 and 270 nm for **1a**, at 230 and 260 nm for **1b** and, at 230 and 270 nm for **1c** are practically identical and can be attributed to  $\pi \rightarrow \pi^*$  transitions in the benzene and benzimidazole ring [34].



Fig. 5. UV-Vis spectra of the compounds 1a-c.

# 3.8 Hirshfeld Surface (HS) Analysis

Hirshfeld surface analysis method was carried out to quantify the intermolecular interactions of the investigated compounds. The Hirshfeld surfaces of **1a-c** are displayed in Fig. S8-10, showing surfaces that have been mapped over a  $d_{norm}$ . The surfaces are shown as transparent to allow visualization of the molecules. The larger red circular regions on  $d_{norm}$  surfaces represent the strong hydrogen bonding interactions. As can be seen from the  $d_{norm}$  map of compound **1a**,

the H···O reciprocal contacts have a pair of adjacent deep-red regions, which is attributed to C1– H1A···O2 hydrogen bonds (Table 2) forming  $R_2^2(12)$  dimers as described in Fig 1b. The strong hydrogen bond interactions O1–H1···I1 and O2–H2···I1 also appear as bright red areas in the Hirshfeld surfaces. Similarly in **1b** and **1c**, the red points, which represent closer contacts and negative d<sub>norm</sub> values on the surface, correspond to the O–H···I hydrogen bonding contacts, are also proven in Table 2. The 2D fingerprint plots of the intermolecular contacts are also shown in Fig. S8-10. For all compounds, the O–H···I hydrogen bonding intermolecular interactions appear as small *spikes*. In the plot of the structure **1a**, there are also two sharp *spikes*, which are identified as a result of C1–H1A···O2 hydrogen bonds. The broad regions at the middle of plots are reflected as H···H interactions comprising 50.3%, 68.0% and 61.6% of the total Hirshfeld surfaces, respectively.

# 4. Conclusion

In this study, three new 2-hydroxyethyl substituted NHC precursors **1a-c** were synthesized, characterized by FT-IR, <sup>1</sup>H, <sup>13</sup>C NMR and UV-Vis spectroscopy. Crystal and molecular structure of the compounds were determined by single-crystal X-ray diffraction method. Structural determination showed that the crystal structure of the compounds is stabilized by O–H···I type hydrogen bonds. Potential energy surface (PES) scans, around the torsion angles ( $\tau$ ) of two sides of the NHC fragments, reveal that global minimum structures are the most stable conformers, and they match well with the experimental one. MEP of the compounds shows that the iodide ion around of the Conf-II of **1b** seems to be the most electron-rich region with the red color for the unfavorable geometry of Conf-II. The intercontacts in the crystal structures of the molecules were also analyzed using the Hirshfeld surface analysis method. For all compounds, all the interaction calculations were found to be in good agreement with the experimental XRD structural parameters.

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# **Supplementary**

Crystallographic data as .cif files for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center with CCDC 1948427 for **1a**, 1948440 for **1b** and 1948441 for **1c**. Copies of the data can be obtained free of charge at <u>http://www.ccdc.cam.ac.uk/conts/retrieving.html</u> or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK, fax: (+44) 1223-336-033. email: <u>deposit@ccdc.cam.ac.uk</u>.

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