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Orthogonal Hydrogen/Halogen bonding in 1-(2-methoxyphenyl)-1H-imidazole-2(3H)-thione-I₂ adduct: An Experimental and Theoretical study

Hamdy S. El-Sheshtawy^{1,3*}, Mohammed M. Ibrahim^{2,4}, Ibrahim El-Mehasseb^{2,3}, Maged El-Kemary^{2,3}

¹Biotechnology and Fish Processing Department, Faculty of Aquatic and Fisheries Sciences, Kafrelsheikh, University, 33516 Kafr ElSheikh, Egypt
²Chemistry Department, Faculty of Science, Kafrelsheikh University, 33516 Kafr ElSheikh, Egypt.
³Nanochemistry Laboratory, Chemistry Department, Faculty of Science, Kafrelsheikh University, 33516 Kafr ElSheikh, Egypt
⁴Chemistre Department, Faculty of Science, Teif University, Teif, See J. Achievent.

⁴Chemistry Department, Faculty of Science, Taif University, Taif, Saudi Arabia

Abstract

The molecular complex between 1-(2-methoxyphenyl)-1H-imidazole-2(3H)-thione $(\text{Hmim}^{\text{OMe}})$ and iodine (I_2) was investigated. Single crystal of $[(\text{Hmim}^{\text{OMe}}) \cdot I_2]$ adduct was grown by slow evaporation technique from chloroform at room temperature. Spectroscopic techniques such as FT-IR and Raman techniques, as well as elemental and thermal analysis were used to characterize the complex. The crystal structure shows that the formed adduct stabilized by two noncovalent interactions, namely, hydrogen bond (HB) and halogen bond (XB). Orthogonal HB/XB associated with iodine atom (I) was observed and fully characterized. The ability of iodine to behave as hydrogen bond acceptor and halogen bond donor was held responsible for the orthogonal HB/XB presence. In addition, the structure of $\text{Hmim}^{\text{OMe}} \cdot I_2$ was investigated theoretically using MP2/aug-cc-pvdz level of theory. Natural bond orbital analysis (NBO) was used to investigate the molecular orbitals interactions and orbital stabilization energies.

Keywords: 1-(2-methoxyphenyl)-1H-imidazole-2(3H)-thione, Halogen bond, Hydrogen bond, X-ray crystal structure, Theoretical calculations.

*Corresponding author:

Tel.: +201062668020, **E-mail:** h.elsheshtawy@fsh.kfs.edu.eg

1. Introduction

The increasing role of noncovalent interactions in different fields such as crystal engineering, molecular recognition, and drug design attracts the interest of researches [1, 2]. In particular, hydrogen bond (HB) and halogen bond (XB) were extensively investigated [1, 3, 4]. Different types of Hydrogen bond (HB) were reported such as conventional HB (Y-H...Z, where Y is electronegative atoms and Z encompass free electron pairs) and unconventional HB (C–H···Y, Y–H···C, Y–H··· π -electrons or even $C-H\cdots C$ [5]. In addition, short-strong hydrogen bond (SSHB) was reported as binding motive in the unique tertiary structures of protein [6, 7]. In analogy, the specific interaction $(C-X \cdots Y)$ between halogen atoms (X=I, Br, and CI) in halogenated ligands and the electron pairs of donor atoms (Y = S, N, O, π -electrons of organic systems) forms the highly directional and linear halogen bond (XB). The charge distribution along the C-X bond is not uniform but rather anisotropic where an increase of charge concentration is found in the plane perpendicular to the C-X bond. On the other hand, the charge deficient is centered on the same axis of the C-X bond, which forms the basis of σ -hole principal [8, 9]. The strength of the XB increases linearly with the size of σ -hole, which manifests the electrostatic nature of these bonds [10-13]. In addition, polarization and dispersion

forces plays a key role in the XB stabilization [11, 12]. The strength of the stabilization energy of HB is frequently higher than that of XB [1], nevertheless, competition between HB and XB was recently reported [14, 15].

The orthogonal molecular interaction between the HB and XB to develop the hXbond was reported by Voth *et al* [16]. In hX-bonds, both hydrogen and halogen atoms share the same acceptor oxygen atom rather than competing to each other. The XB were perpendicular to HB with a maximum bond angle of 88.2° and energetically independent of the HB. The orthogonality principal was first reported in the interaction between ligands and proteins [16] and subsequently confirmed for different systems [17, 18]. Similarly, halogen atom can possesses the dual nature as the HB acceptor and XB donor. On one hand, halogen atom possesses loan pair of electrons, which could be the motive for HB interaction; on the other hand the presence of σ -hole along the bond axis leads to the XB donor nature of the halogen atom [19].

Herein, we synthesized a new 1-(2-methoxyphenyl)-1H-imidazole-2(3H)-thione (Hmim^{OMe}) , which could have pharmaceutical importance. The molecular structure of Hmim^{OMe} and its molecular adduct with I₂ was investigated with different spectroscopic techniques such as FT-IR, FT-Raman, elemental analysis and thermal analysis. Single crystal of $\text{Hmim}^{OMe} \cdot I_2$ was grown and the structure was investigated both theoretically and experimentally. Theoretical calculations using both MP2/aug-cc-pVDZ-PP and B3LYP/6-311++G(d,p) level of theory were corroborated the experimental results to shed more light on both Hmim^{OMe} and $\text{Hmim}^{OMe} \cdot I_2$ molecular structures.

2. Experimental

2.1. Materials and methods

Infrared spectral measurements (FT-IR) for the free thione and the molecular adduct with iodine were recorded in KBR pellets using FT-IR Prestige-21 Shimadzu, in the range of 400-4000 cm⁻¹. Raman spectra were obtained as powder in glass capillaries on a Nicolet FT Raman-950 spectrophotometer. The spectra were recorded at room temperature with a germanium detector, maintained at liquid nitrogen temperature and using 1064.0 nm radiation, generated by a Nd-YAG laser with a resolution of 2 cm⁻¹. Thermal analysis of the complex was recorded on Netzsch STA 449F3 with system interface device in the atmosphere of nitrogen. The temperature scale of the instrument was calibrated with high purity calcium oxalate. Accurately 5 mg of pure sample was subjected for dynamic TG scans at heating rate of 10 °C min⁻¹.

2.2 Computational details

All calculations were performed using Gaussian03 program [20]. In case of Hmim^{OMe}-I₂, Dunning's correlation-consistent polarized valence double-zeta basis set augmented with diffuse functions and employing pseudo potentials to describe the inner core orbitals of the heavy-atom elements, I, (aug-cc-pVDZ-PP) was employed in the *abinito* calculations. The energies were obtained by using second order Møller–Plesset perturbation theory (MP2), with and without counterpoise (CP) correction for basis set superposition errors (BSSE). The use of larger basis set in addition to the CP corrections usually, for BSSE, results in overestimation of the binding

energies. The parent compound ($Hmim^{OMe}$) was optimized at B3LYP/6-311++G(d,p) level of theory, which gives satisfactory results compared to the experimental data [21]. Analytical frequency calculations were done in order to verify the stationary points on the potential energy surface. Natural population analysis (NPA) was used to calculate the natural bond orbital interactions and their second-order perturbation stabilization energies (E^2) at MP2/ aug-cc-pVDZ-PP level of theory.

2.3. Syntheses

2.3.1. Synthesis of 1-(2-methoxyphenyl)-1H-imidazole-2(3H)-thione (Hmim^{OMe})

The ligand 1-(2-methoxyphenyl)-1H-imidazole-2(3H)-thione (Hmim^{OMe}) was prepared according to a modified procedure reported in literature [22-24] (Scheme 1). In details, N-(2,2-diethoxyethyl)-2-methoxyaniline (30.63 g, 0.128 mol)) in ethanol (130 mL) were mixed with 14.90 g (0.153 mol) of potassium thiothianate, to which 75 mL of HCl (2N) were added. The reaction mixture was refluxed for 24 hrs and the solvent was removed by rotatory evaporator. A hot water (500 ml) was added to the residue with continuous stirring. After cool down, a raw product was obtained as pale yellow solid, which filtered, dried, and crystallized from ethanol by using activated charcoal. Anal. For C₁₀H₁₀N₂SO (206.26): Calcd. C, 58.32; H, 4.89; N, 13.58; S, 15.54; Found C, 58.02; H, 4.93; N, 13.64; S, 15.44. ¹H NMR (DMSO), 298 K, TMS): δ = 3.82 [s, 3H, CH₃], 6.92 [d, 1H, H³-thioimidazole], 7.14 [d, 1H, H²thioimidazole], 7.29-7.43 [m, 4H, Ph] and 12.21 ppm [b, 1H, NH]. I R (KBr): ν (cm⁻¹): 3088 [s, br, NH], 1567 [s, -C=C-], 1502 [s, C=N], 1446 [s, Thioamide I], 1278 [s,

Thioamide II], 1014 [m, thioamide III], 727 and 676 [s, Thioamide IV], 613 [m, δ (C=S)], and 531 [s, π (C=S)].



Scheme 1. The synthesis of 1-(2-methoxyphenyl)-1H-imidazole-2(3H)-thione (Hmim^{OMe})

2.3.2. Synthesis of the CT complex 1-(2-methoxyphenyl)-1H-imidazole-2(3H)-thione. Iodine [$Hmim^{OMe} \cdot I_2$]

A chlorofrm solution (10 mL) containing iodine solution (1.0 mmol, 0.254 gm) was added to a chlorofrm solution (10 mL) of the donor 1-(2-methoxyphenyl)-1H-imidazole-2(3H)-thione (1.0 mmol, 0.206 gm). Immediately, a brown solution was obtained, which was kept standing for 3 days. Single brown crystals were obtained of the Hmim^{OMe}•I₂ adduct, which were washed and crystallized from cold chloroform. Anal. For C₁₀H₁₀N₂SOI₂ (460.07): Calcd. C, 26.11; H, 2.19; N, 6.09; S, 6.97; Found C, 25.87; H, 2.08; N, 6.24; S, 6.73. ¹H NMR (DMSO), 298 K, TMS): δ = 3.87 [s, 3H, CH₃], 6.97 [d, 1H, H³-thioimidazole], 7.18 [d, 1H, H²-thioimidazole], and 7.34-7.55 ppm [m, 4H, Ph]. IR (KBr): v (cm⁻¹): 3116 [s, br, NH], 1553 [s, -C=C-], 1499 [s, C=N], 1424 [s, Thioamide

I], 1244 [s, Thioamide II], 1012 [m, thioamide III], 742 and 679 [s, Thioamide IV], 620 [m, δ (C=S)], and 515 [s, π (C=S)].

2.4. X-Ray Crystallography

Crystallographic data of Hmim^{OMe}•I₂ were collected on a Smart CCD diffractometer of Bruker AXS using Mo Ka radiation. The crystal does not show significant intensity loss through data collection. Lorentz-Polarization corrections were performed by SAINT [25]. Absorption corrections were made by using SADABS [26]. The structure was solved by direct or Patter- son methods using SHELXS-97 [27] to find the position of heavy atoms. Other non-hydrogen atoms were located by Fourier syn- theses and refined using SHELXS-97. The least-squares refinements were performed using all independent reflections by the full matrix on F2. All non-hydrogen atoms were refined anisotropically. X-ray diffraction study was carried out using XRD-6000 (SHIMADZU). The X-ray was detected using a fast counting detector based on silicon strip technology. The crystal structure and lattice parameter were analyzed by Bragg's law, 2dsin θ = n λ and particle size is calculated by Debye Scherer's formula, t = 0.9 λ /B cos θ [28, 29].

3. Results and discussions

3.1. Molecular structures and X-Ray investigation

The structure of 1-(2-methoxyphenyl)-1H-imidazole-2(3H)-thione (Hmim^{OMe}) [22-24] was synthesized *via* the ring closure of N-(2,2-diethoxyethyl)-2-methoxyaniline and potassium thiocyanate in ethanol and HCl (2N). The obtained thioimidazole was crystallized from ethanol to form colourless crystals (Scheme 1). Crystals of Hmim^{OMe}•I₂

adduct were produced by co-crystallising Hmim^{OMe} with the appropriate concentration of iodine in chloroform to give the 1:1 stoichiometric ratio.

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	Compound	Thione
	Empirical formula	$C_{10}H_9I_2N_2OS$
	Formula weight, g/mol	459.06
	Crystal system	Triclinic
	Space group	P -1
	aĺÅ	7.2897 (3)
	b/Å	9.0456 (4)
	c/Å	11.6315 (6)
	α/°	69.181 (2)°
	βI°	76.782 (2)°
	γ/°	80.439 (3)°
	Volume/Å3	694.87 (6)
	Z	2
	$D_{\rm calc}/({\rm g/cm3})$	2.199
	Absorption coefficient	
	F(000)	426.0
	Crystal size/mm	8,10,13
	\rightarrow range for data collection/°	2.910—32.032 °
	Reflections collected	4952
	Independent reflections	4731
	R(int)	0.029
	Observed $(I > 2 \leftrightarrow (I))$	
	Goodness-of-fit on F2	1.0
	$R[I > 2 \leftrightarrow (I)]b$	
1	w P (all data) c	0.0756

The crystallographic data of $\text{Hmim}^{\text{OMe}} \cdot I_2$ are collected in Table 1. Careful examination of the $\text{Hmim}^{\text{OMe}} \cdot I_2$ crystal structure indicates the presence of two XB bonds associated with the S atom, but has different strength due to the orthogonal HB, which

linked two successive layers (Fig.1). In addition, the crystal structure sheets are connected with a short contact between the C…C bond (3.38 Å, 0.6 % less than vdW radii).



Fig. 1: Halogen bond and hydrogen bond motif of Hmim^{OMe}•I₂.



Fig. 2: Intermolecular interactions, and bond lengths (Å) in crystalline structure of $Hmim^{OMe} \bullet I_2$ adduct

bond distance /Å		bond ang	gle/°	torsional angle/°		
I1–S5	2.579(1)	S5-I1-I16	174.87(3)	I16-I1-S5-C2	-163.6(3)	
I1–I16	2.9966(4)	S5-C2-N8	128.0(3)	N8-C2-S5-I1	70.1(4)	
C2-S5	1.718(4)	S5-C2-N10	126.2(4)	N10-C2-S5-I1	-111.6(4)	
C2-N8	1.348(5)	N8-C2-N10	105.7(4)	S5-C2-N8-C11	-2.0(6)	
C2-N10	1.331(5)	C7–C3–C12	120.7(5)	S5-C2-N8-C14	179.9(4)	
C3–C7	1.371(9)	С7-С3-Н25	122(3)	N10-C2-N8-C11	179.5(4)	
C3-C12	1.395(5)	С12-С3-Н25	118(3)	N10-C2-N8-C14	1.4(5)	
C3-H25	0.88(6)	C9-O4-C12	117.7(4)	S5-C2-N7-C15	-179.4(4)	
O4–C9	1.430(8)	I1-S5-C2	101.1(2)	S5-C2-N10-H21	-10(6)	
O4–C12	1.341(6)	C11-C6-C13	119.4(5)	N8-C2-N10-C9	-0.8(5)	
C6–C3	1.379(8)	С11-С6-Н23	110(3)	N8-C2-N10-H21	169(6)	
C6-C13	1.378(7)	С13-С6-Н23	130(3)	С12-С3-С7-С13	-0.3(8)	
C6-H23	0.89(5)	C3–C7–C13	121.4(5)	С12-С3-С7-Н21	-179(3)	
C7–C13	1.37(1)	С3–С7–Н19	123(3)	H25-C3-C7-C13	179(4)	
C7-H19	0.99(4)	С13-С7-Н19	115(3)	С7-С3-С12-О4	179.6(5)	
N8-C11	1.442(5)	C2-N8-C11	125.7(3)	C7-C3-C12-C11	-1.4(7)	
N8-C14	1.387(6)	C2-N8-C14	109.7(4)	С9-04-С12-С3	-6.9(6)	
C9-H24	0.93(5)	C11-N8-C14	124.5(4)	C9-O4-C12-C11	174.1(4)	
C9-H18	1.15(7)	O4-C9-H24	111(4)	C13-C6-C11-N8	179.9(5)	
C9–H17	1.01(4)	O4-C9-H18	104(3)	C13-C6-C11-C12	-2.2(7)	
N10-C15	1.366(7)	O4-C9-H17	107(3)	C11-C6-C13-C7	0.4(8)	
N10-H21	0.77(5)	C2-N10-C15	110.6(4)	С3-С7-С13-С6	0.8(9)	
C11-C12	1.402(7)	C2-N10-H21	128(5)	C2-N8-C11-C6	-105.8(5)	
С13-Н22	0.82(7)	C15-N7-H21	121(5)	C2-N8-C11-C12	76.2(5)	
C14-C15	1.332(6)	C6-C11-N8	119.5(4)	C14-N8-C11-C6	72.0(6)	
C14-H20	0.92(4)	C6-C11-C12	121.9(4)	C14-N8-C11-C12	-105.9(5)	
С15-Н26	0.81(4)	N8-C11-C12	118.6(4)	C2-N8-C14-C15	-1.5(5)	

Table 2: Selected bond lengths, bond angles and torsional angles of $\text{Hmim}^{\text{OMe}} \bullet I_2$ molecular adduct.

In details, the crystal structure of $\text{Hmim}^{\text{OMe}} \cdot I_2$ shows a short and linear C=S2…I2 interaction (Fig. 2). The S2…I2 bond distance is 2.579 Å, which is 31.8 % shorter than

the sum of vdW radii of both S (1.80 Å) and I (1.98 Å) atoms. The S2…I2-I1 bond angle is 174.87°, which is matching the linearity of the XB [30]. On the other hand, the S2…I3 bond distance is 3.697 Å, which is 2.2 % shorter than the sum of vdW radii for both I and S atoms, and the bond angle (I3…S2-I1) is 152.11°. The weakness and deviation from linearity of I3…S2 than the S2…I2 XB can be explained by the interference of the strong I1…H2-N1 HB, the I1…H2 bond distance is 2.80 Å (12 % less than vdW radii) and I1…H2-N1 bond angle is 171.93° [31]. Selected geometry parameters according to the single crystal structure (Fig. 3) are in Table 2.



Theoretical calculations using both B3LYP/6-311++G(d,p) and MP2/aug-cc-pVDZ-PP level of theory were corroborated to further investigate the structure of both

and $\operatorname{Hmim}^{OMe} \bullet I_2$. The relative calculated energies (B3LYP/6-311++G(d,p)) Hmim^{OMe} shows that thione form (Hmim^{OMe}-I) was more stable by 4.5 kcal mol⁻¹ than thiol form (Hmim^{OMe}-II). Electrostatic potential V(r) that electrons and nuclei of a molecule create at any point (r) is an effective method for interpreting and quantifying noncovalent interactions [32]. Here, we compute the electrostatic potential surface (EPS) of both Hmim^{OMe}-I and Hmim^{OMe}-II to investigate the electron density distribution. Fig. 4 displays the positions of the concentrated and deficient electron densities located on the two isomers as well as the I₂ molecule. EPS shows the presence of a strong negative potential $(-37.65 \text{ kcal mol}^{-1})$ situated around the S atom in Hmim^{OMe}-I isomer. The symmetrically high negative potential distributed over the S atom facilitates the contacts with two Lewis acid atoms (two I atoms in crystal structure). In contrast, a weak negative electrostatic potential (- 9.05 kcal mol⁻¹) were observed on the S in the Hmim^{OMe}-II structure and increases at the two N atoms of the imidazole moiety. Interestingly, relatively high positive potential $(+25.2 \text{ kcal mol}^{-1})$ were centered on the H atom of N-H bond, which is the motif forces for the HB formation. On the other hand, ESP of the I₂ molecule nicely visualizes the σ -hole principal, where a strong positive electrostatic potential $(+40.45 \text{ kcal mol}^{-1})$ is formed along the I-I bond axes. Such electron deficient region was found in the covalently chlorinated, brominated, and iodinated organic molecules [33, 34]. Perhaps, the most interesting region in I_2 ESP is the negative electrostatic potential (-29.15 kcal mol⁻¹) belt perpendicular to the I-I bond axes. The propensity of the negative electrostatic potential ($-29.15 \text{ kcal mol}^{-1}$) belt on I₂ molecule

and the positive electrostatic potential (+25.2 kcal mol^{-1}) found on the H atom of N-H bond forms HB, I1...H2 bond distance is 2.80 and 171.93° bond angle (I1...H2-N1).



Fig. 4: a) calculated structure of Hmim^{OMe} -I and Hmim^{OMe} -II using B3LYP/6-311++G(d,p), b) the ESP of the optimized structure, c) ESP of I₂ optimized at MP2/augccp-pvdz, d) ESP of Hmim^{OMe} •I₂ (single energy calculation at MP2/aug-ccp-pvdz) color codes, blue (positive), red (negative).

In order to give more insights to the complex, natural bond orbital analysis (NBO) were performed at MP2/aug-cc-PVDZ level of theory. Table 3 shows selected bonding, antibonding, and lone pair interaction orbitals as well as the second-order perturbation stabilization energies (E^2). NBO analysis reveals the strong stabilization from the lone pair electrons of the S atom to the σ^* of the I₂ molecule (LP(3) S5 \rightarrow BD*(1) I1 - I16) with E(2) = 163.58 kcal/mol. This result confirms the n- σ^* nature of the transition similar to compounds incorporate thion (C=S) group. Strong stabilization energy manifests the role of the charge transfer for the Hmim^{OMe}•I₂ complex [35]. In fact, the charge transfer to the antibonding orbital of I1 - I16 bond weaken and consequently lengthen [36, 37] the I1 -116 bond length: the I1 - I16 bond length in crystal structure is 2.9966 Å, which is 0.2766 Å longer than the I–I bond in crystalline I₂ (2.72 Å) [38]. Interestingly, a strong intramolecular interaction was observed from the LP (1) N8 \rightarrow LP*(1) C2 and LP (1) $N10 \rightarrow LP^{*}(1)$ C2 with strong stabilization energy of 206.82 and 179.87 kcal/mol respectively, which manifests the role of the intramolecular charge transfer in the stabilization of adduct [35, 39].

Table 3: Some significant donor-acceptor (D \rightarrow A) natural bond orbital interactions and 14

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$D \rightarrow A$	$E^{(2)}$	E(j)-E(i) a.u.	F(i,j) a.u.	
BD (1) I1 - I16	BD*(1) I1 - I16	2.77	0.39	0.033
LP (1) I1	BD*(1) I1 - I16	3.80	0.90	0.058
LP (2) I1	BD*(1) I1 - I16	0.51	0.37	0.013
LP (3) I1	BD*(1) I1 - I16	0.78	0.38	0.017
BD (1) I1 - I16	RY*(1) S5	2.72	1.39	0.055
LP (3) I1	BD*(1) C2 - S5	1.88	0.84	0.036
BD (1) C2 - S5	BD*(1) I1 - I16	1.18	0.90	0.032
LP (1) S5	BD*(1) I1 - I16	11.93	0.83	0.098
LP (2) S5	BD*(1) I1 - I16	2.86	0.34	0.030
LP (3) S5	BD*(1) I1 - I16	163.58	0.32	0.212
BD (1) N8 - C14	BD*(1) C2 - S5	5.46	1.49	0.080
LP (1) S5	BD*(1) C2 - N8	8.38	1.55	0.102
LP (2) S5	BD*(1) C2 - N10	14.68	1.08	0.114
LP (3) S5	LP*(1) C2	82.77	0.23	0.134
LP (3) S5	BD*(1) C2 - N10	2.29	1.07	0.050
LP (1) N8	LP*(1) C2	206.82	0.27	0.236
LP (1) N10	LP*(1) C2	179.87	0.31	0.236

their second-order perturbation stabilization energies (E^2) , in kcal/mol) at the MP2/augcc-pVTZ level^a

3.2. Characterization of the CT complex

The reaction of 1-(2-methoxyphenyl)-1H-imidazole-2(3H)-thione with iodine in 1:1 molar ratio in chloroform readily produced the crystalline CT complex $Hmim^{OMe} \cdot I_2$. The elemental analysis of the complex confirmed the 1:1 stoichiometry and physical properties is in accordance with the proposed structure. In order to investigate the molecular interactions, different spectroscopic techniques such as FT-IR, FT-Raman, and thermal analysis were used.

^aLP denotes the occupied lone pair. BD* denotes the formally empty antibonding orbital. RY* denotes Rydberg orbital.

3.2.1 FT-IR and Raman Spectra

The FT-IR spectrum of $\text{Hmim}^{\text{OMe}} \cdot I_2$ adduct (Fig. 5) shows the absence of v(SH)band at 2500 cm⁻¹ and the presence of v(NH) band at 3116 cm⁻¹, which clearly reveals the dominance of Hmim^{OMe}-I (thione) structure in solid. Upon complexation of Hmim^{OMe} with I₂, the v(C=S) absorption was shifted from 759 cm⁻¹ to 742 cm⁻¹. The shift of v(C=S)absorption to 742 cm^{-1} ascribed to the change of C=S electronic state; loses some of the double bond character and lengthen the C-S bond distance (Table 2). The thioamide bands are shifted, however the most significant change was that observed in the thioamide IV bands, which have the largest shift to lower frequency [40, 41]. The thioamide IV band is affected with the bands in the free ligand (759 and 730 cm^{-1}), which are replaced by a sharp band at 741 and 673 cm^{-1} for the complex. Besides, the electron charge-transfer between the S atom of a thioamide and iodine will result in stabilization of the lone pair of electrons on the S atom by overlapping of the S donor orbital with the σ^* -orbital of iodine [42]. This situation will lead to a lengthening of the thione double bond in the thioamide and subsequent bond formation between the S atom and diiodine, together with a concomitant lengthening of the I–I bond.

The FT-Raman spectra of $\text{Hmim}^{OMe} \cdot I_2$ in the 90 – 4000 cm⁻¹ region was investigated (Fig. 6. Shows selected region from 0 - 600 cm⁻¹). The spectra show an intense peak at 177 cm⁻¹, which attributed to the uncomplexed I₂. As expected, the v(I–I) value in the molecular adduct was shifted to lower frequency value from the v(I–I) of the solid I₂ (180 cm⁻¹). The lower frequency value is associated with the increase of the I – I bond length (2.99 nm) compared of the free I – I bond length in the solid state. Further, 16

two peaks were observed at 80, 109 cm⁻¹, which ascribed to the $v(I_3^-)$, and $v_s(I-I)$ respectively.



Fig. 5: FT-IR spectra of a) Hmim^{OMe} , and b) Hmim^{OMe} -I₂ adduct.



Fig. 6: Selected Raman spectra of the $\text{Hmim}^{\text{OMe}} \cdot I_2$ molecular adduct.

3.3.Thermal analysis

The structure of Hmim^{OMe} and it's adduct with I₂, $\text{HmimOMe} \cdot I_2$, were also characterized by thermal analysis. Fig. 7a displays the collected TGA, DTG, and DSC curves for the thermal decomposition of Hmim^{OMe} . The TGA curve exhibits one weight loss step with a mass loss of 93.09% (calcl. 91.27%), which is mainly due to the decomposition of Hmim^{OMe} forming 1.5 mole of solid carbon. The DSC curve shows three main events at 238.1 °C (exo), 318.6 °C (exo), and 591.8 °C (endo). The first exothermic peak is accompanied by no weight loss, which suggests a physical process (possibly ligand melting). The second exothermic peak is attributed to the decomposition of Hmim^{OMe} . The third endothermic peak with no weight loss change attributed to the recrystallization of the final carbon product.

Sample	Step	Т	А	ΔE^*	ΔH^*	ΔS^*	ΔG^*
Hmim ^{OMe}	1^{st}	533	16.6557	107.71	104.795	-0.1113	164.107
							0
$Hmim^{OMe} \bullet I_2$	1^{st}	588	8.9093	69.444	66.5262	-0.1766	170.314
	2^{nd}	1038	10.2909	1.9124	1.0058	-0.1698	177.206

Table 4: Kinetic and thermodynamic parameters of the $\operatorname{Hmim}^{OMe}$ and $\operatorname{Hmim}^{OMe} I_2$

Fig. 7b displays the collected TGA, DTG, and DSC curves for the thermal decomposition of the Hmim^{OMe}•I₂ adduct. The TGA curve exhibits three weight loss steps with a total mass loss of 85.01% (calc. 84.35%), due to the decomposition of Hmim^{OMe}•I₂ forming 6.0 mole of carbon. The DSC curve shows three main events, which are maximized at 149.4 °C (exo), 289.1 °C (exo) and 628.2 °C (exo). The first exothermic peak is accompanied by no weight loss, which suggests a physical process (possible melting of the complex). The second and third exothermic peaks are attributed to the decomposition of the complex. The kinetic ($\Delta E^{#}$) and thermodynamic parameters ($\Delta S^{#}$, $\Delta H^{#}$, and $\Delta G^{#}$) for the decomposition of Hmim^{OMe} and Hmim^{OMe}•I₂ were calculated by Coats–Redfern equation [43]. The negative values (Table 4) of more entropies in Hmim^{OMe}•I₂ indicate that the activated complex has more ordered structure than the reactants [44]. In addition, thermal analysis reveled the stabilization of the iodinated adduct than the reactant (Hmim^{OMe}).



Fig. 7: TGA (black), DTG (red), and DSC (blue) curves of the Hmim^{OMe} (a) and $\text{Hmim}^{\text{OMe}} \cdot I_2$ (b).

Conclusion

The new compound, 1-(2-methoxyphenyl)-1H-imidazole-2(3H)-thione (Hmim^{OMe}), was synthesized and structurally investigated. The molecular interaction between Hmim^{OMe} and molecular iodine (I₂) were discussed. The crystal structure reveals the presence of orthogonal hydrogen and halogen bonding associated with iodine atom (I). The reason for such orthogonality was ascribed to the presence of negatively charged belt perpendicular to the I-I bond in addition to the positively charged region (σ -hole) in the same plane with the I-I bond. Theoretical calculations, using NBO analysis, confirms the n- σ * nature of the charge transition from the S atom to I atom in the molecular adduct. In addition, spectroscopic techniques such as FT-IR and Raman techniques were used to further investigate the adduct formation.

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Highlights

- Synthesis of 1-(2-methoxyphenyl)-1H-imidazole-2(3H)-thione (Hmim^{OMe}). ٠
- Orthogonal Hydrogen bond (HB) and halogen bond (XB) in Hmim^{OMe}•I₂ crystal structure. •
- Spectroscopic and thermal investigation of Hmim^{OMe}•I₂ adduct.