Scientific paper

Spectroscopic and Electrochemical Observation of Hydrogen-Bonded Imidazole and 2-Aminoimidazole Clusters

Nuran Özçiçek Pekmez,[a,]* Muzaffer Can,[b] Attila Yildiz[a]

[a] *Hacettepe University, Department of Chemistry, 06532, Beytepe, Ankara, Turkey.*
Fax: +903122992163, E-mail: npekmez@hacettepe.edu.tr.

[b] *Department of Chemistry, Gaziosmanpasa University, 60250 Tasliciftlik, Tokat, Turkey*

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Abstract

The electroreductions of imidazole and 2-aminoimidazole were investigated on a Pt electrode in acetonitrile containing tetrabutylammonium tetrafluoroborate with and without the presence of HBF_4. The effects of lithium and tetrabutylammonium ions on the electroreduction and FTIR and ^{1}H NMR results were also compared. The feasibility of the formation of intermolecular hydrogen bonds was elucidated by the use of the theoretical calculations. Electroreduction waves were interpreted by the existence of the hydrogen-bonded clusters in acetonitrile containing tetrabutylammonium tetrafluoroborate.

Keywords: imidazole, 2-aminoimidazole, hydrogen bond, NMR, FTIR, theoretical investigation

1. Introduction

Hydrogen bonds are relatively weak interactions between molecules and yet they are of paramount importance in chemistry and pivotal in determining biomolecular structure and function. This type of interactions governs many biologically important processes in which the enzymatic catalysis is particularly relevant.[1–3] R. Vianello et al. performed a comparative spectroscopic FTIR and computational study of the vibrational OH stretching frequencies in liquid ethanol-ethanol and liquid ethanol-*N*-methylimidazole dimmers.[4] The latter system mimics the hydrogen bond formation between serine and histidine residues, which is the incipient step in the enzymatic activity of the catalytic triads. The infrared spectra revealed the presence of the OH fundamental stretching transitions at 3339 and 3271 cm^{-1} for ethanol dimers and ethanol-*N*-methylimidazole dimers, respectively. This red shift of 68 cm^{-1} indicates that the hydrogen bond between ethanol and *N*-methylimidazole exists and it is favoured over the one occurring in ethanol dimers. It is shown that vibrations exhibit anharmonicity.

IR spectroscopic studies in carbon tetrachloride solution verified the formation of hydrogen-bonded oligomers.[5] It was observed in another IR spectroscopic investigation that the tetraalkylammonium salts promotes the formation of the hydrogen-bonded chains from the compounds that can form hydrogen bonds.[6] Some 2-substituted benzimidazoles and their 1-methyl derivatives were investigated theoretically with respect to their tendency to form an intramolecular hydrogen bond.[7]

Interactions between phenol and the tetramethylammonium (TETMA) ion were studied experimentally by measuring electrolyte conductivity and its dielectric constant and theoretically using the HF/6-31G(d) and B3LYP/6-31G(d) ab-initio levels of theory. In the latter study, the effect of aqueous environment was included by using the solvent reaction field method. The experiment and the theory give evidence for the existence of complexes between phenol and the TETMA ion in aqueous solution.[8]

In the presence of urea the electroreduction of *o*-quinones was observed at more positive potentials due to the formation of hydrogen bonds between quinone and urea.[9] The effect of the hydrogen bond formation causes large positive shifts on the electroreduction potentials and negative shifts on the electrooxidation potentials of some inorganic complex ions.[10,11]

The electroreduction behaviour of imidazole, 1-methylimidazole, 4,5-diphenylimidazole, 2,4,5-triphenylimidazole (Lophine), benzimidazole, 2-methlybenzimidazole, 2,2'-bisbenzimidazole and benzdiimidazole on Pt electrode in acetonitrile containing tetrabutylammonium perchlorate (TBAP) was interpreted using cyclic voltammetric and controlled potential electrolysis results only.[12] In a solution containing TBAP a broad reduction peak was observed whereas no reduction process was detected in $LiClO_4$ solution. The results were interpreted by the existence of hydrogen- bonded clusters in acetonitrile solution. These clusters are formed if tetraalkylammonium salts are used as a supporting electrolyte. The presence of lithium salts in solution inhibits the formation of such clusters because of the interaction of lithium with the nonbonding electrons on the nitrogen centers of the imidazole ring which prohibits the electroreduction.

In a previous study, the electroreduction of benzimidazole, 5-aminobenzimidazole and 4- aminobenzimidazole were investigated on a Pt electrode in acetonitrile containing tetrabutylammonium tetrafluoroborate ($TBABF_4$) with and without the presence of HBF_4.[13] The presence of a proton donor gives rise to the catalytic reduction of protons through various types of protonated benzimidazoles at less negative potentials than those of the neutral hydrogen-bonded benzimidazole clusters. The effect of intermolecular hydrogen bonding on the electroreduction behaviour was elucidated. The feasibility of the formation of the proposed hydrogen bonding was supported by theoretical calculations.

In this study the electroreduction behavior of imidazole and 2-aminoimidazole (2-ai) in acetonitrile/$TBABF_4$ in the presence and absence of HBF_4 was investigated. The experimental results were explained with ^{1}H NMR and FTIR spectral data and theoretical calculations.

2. Experimental

Imidazole (BDH) was purified by vacuum sublimation at 80 °C before use. 2-aminoimidazole was synthesized from the 2-aminoimidazole sulphate (Fluka). 2-aminoimidazole sulphate was dissolved in acetonitrile and then NH_3 was passed through this solution. Diethylether complex of tetrafluoroboric acid (HBF_4, Aldrich) were kept at –10 °C in darkness under a nitrogen atmosphere and used directly. Tetrabutylammonium tetrafluoroborate ($TBABF_4$) was used as a supporting electrolyte. $TBABF_4$ was prepared by reacting tetrafluoroboric acid (Aldrich) with a 40% aqueous solution of tetrabutylammonium hydroxide (TBAOH, Aldrich). It was recrystallized from 70% ethanol several times and kept in a nitrogen atmosphere after vacuum drying for 24 h at 120 °C. $LiBF_4$ (Aldrich) and acetonitrile (Merck) were used directly without any purification. Acetonitrile was purged with nitrogen prior to use.

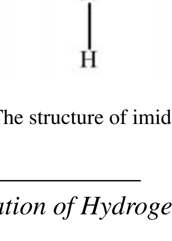
Electrochemical measurements were carried out under a nitrogen atmosphere in three-electrode cell. A polished Pt-disk electrode with a diameter of 0.13 cm inlayed in a glass capillary was used in cyclic voltametric experiments as a working electrode. The counter electrode was a Pt wire (2 cm^2) immersed in acetonitrile/0.1 mol L^{-1} $TBABF_4$ solution, separated from the electrolysis solution by a sintered glass disc (G 4). The reference electrode consisted of an AgCl-coated Ag wire in acetonitrile/0.1 mol L^{-1} $TBABF_4$ solution which was also separated from the electrolysis solution by a sintered glass disc. Electrochemical instrumentation consisted of a PAR Model 173 potentiostat coupled to a PAR Model 175 universal programmer and a PAR Model 179 digital coulometer. Current-voltage curves were recorded on a Model SE-790 BBC Goertz Metrawatt X-Y recorder. The nuclear magnetic resonance (^{1}H NMR) spectra were measured in deuterated chloroform (Merck) on a Bruker 400 MHz spectrometer. The peak at 7.28 ppm belongs to deuterated chloroform proton in all ^{1}H NMR spectra. FTIR spectra of imidazole and 2-aminoimidazole in acetonitrile containing tetrabutylammonium tetrafluoroborate and lithium tetrafluoroborate were measured on a Perkin-Elmer infrared spectrometer.

Theoretical calculations were performed using abinitio (Minimal (STO-3G)) and semi-empirical Austin Model 1 (AM1) in the Hyperchem 7.5 program package with a Pentium III 600 MHz computer.[14,15] This method was used to investigate the aromatic character of compounds, to study some complex structures (such as polymers) and investigate the formation of hydrogen bonds between molecules. The hydrogen bonds lengths were computed after AM1 geometrical optimization.

3. Result and Discussion

Figure 1a shows the cyclic voltametric reduction behavior of imidazole in acetonitrile containing tetrabutylammonium tetrafluoroborate ($TBABF_4$) as supporting electrolyte. A broad cyclic voltametric peak at around –1.77 V vs Ag/AgCl was recorded for the electrodeduction of imidazole. In acetonitrile /0.1 mol L^{-1} $LiBF_4$, there is no reduction peak of imidazole between +0.10 V and –1.90 V vs. Ag/AgCl (Figure 1b).

Figure 2 shows ^{1}H NMR spectrum of imidazole in deuterated chloroform. As seen in this spectrum, there are three signals corresponding to three different protons in imidazole ring (Formula 1). The peak at 7.15 ppm belongs to two equivalent C–H protons on 4 and 5 positions and the peak at 7.73 ppm belongs to C–H proton on position 2. The peak belonging to N–H proton appears at 11.62 ppm.



Formula 1. The structure of imidazole.

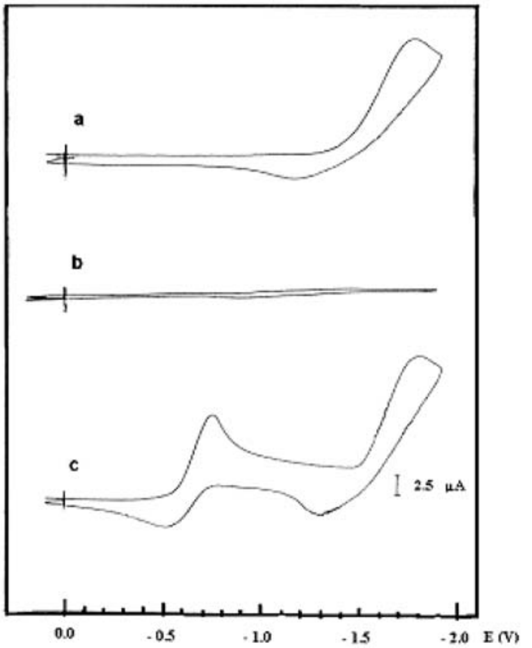


Figure 1. The cyclic voltammograms of a) acetonitrile/0.1 mol L^{-1} $TBABF_4$ solution containing 5 mmol L^{-1} imidazole; b) acetonitrile/0.1 mol L^{-1} $LiBF_4$ solution containing 5 mmol L^{-1} imidazole; c) acetonitrile/0.1 mol L^{-1} $TBABF_4$ solution containing 5 mmol L^{-1} imidazole + 5 mmol L^{-1} HBF_4. Scan rate: 100 mV sec^{-1}.

These chemical shift values are in agreement with the literature values.[16,17]

Figure 3 a and b show ^{1}H NMR spectra of imidazole in acetonitrile-deuterated chloroform mixture containing $LiBF_4$ and $TBABF_4$, respectively. There are two singlet peaks belonging to C–H protons in the imidazole ring at 6.76 ppm (H in 4 and 5 positions) and 7.36 ppm (H in 2 position) in a solution containing $LiBF_4$ (Figure 3a). The similar peaks appear at 6.73 ppm (H in 4 and 5 positions) and 7.30 ppm (H in 2 position) in a solution containing $TBABF_4$ (Figure 3b). A small shift of these peaks towards lower fields implies the existence of some interaction of nonbonding electrons with lithium cations. The peak recorded at 6.76 ppm in medium containing $LiBF_4$ (Figure 3a) and at 6.73 ppm in medium containing $TBABF_4$ (Figure 3b) which belong to two equivalent C–H protons in 4 and 5 positions of imidazole appears as singlet because of the tautomerization equilibrium (Scheme 1).

Scheme 1. The tautomerization equilibrium of imidazole.

As seen in Figure 3a, the broad peak of the N–H proton of imidazole ring in medium containing $LiBF_4$ appears at 6.10 ppm. On the other hand, the broad peak of the same N–H proton in medium containing of $TBABF_4$ is shifted to 10.18 ppm (Figure 3b). TBA^+ cation does not interact with the pyrrole ring because of its much larger size and steric effect. This large difference in the chemical shift values in two media is due to the strong interaction of nonbonding electrons on the nitrogen of the imidazole ring with lithium cations, which prohibits the formation of intermolecular hydrogen bonding. In a medium containing $TBABF_4$, the N–H and N centers on the neighboring rings are utilized for hydrogen-bonded cluster formation. In other words, proton is exchanged between two imidazole rings via the hydrogen bond (Scheme 2), so the N–H proton peak is shifted to much lower field (10.18 ppm). This higher chemical shift value indicates that the proton is held much more weakly by two imidazole rings. The singlet peak due to two equivalent ring protons at 6.73 ppm also gives an evidence for this intermolecular hydro-

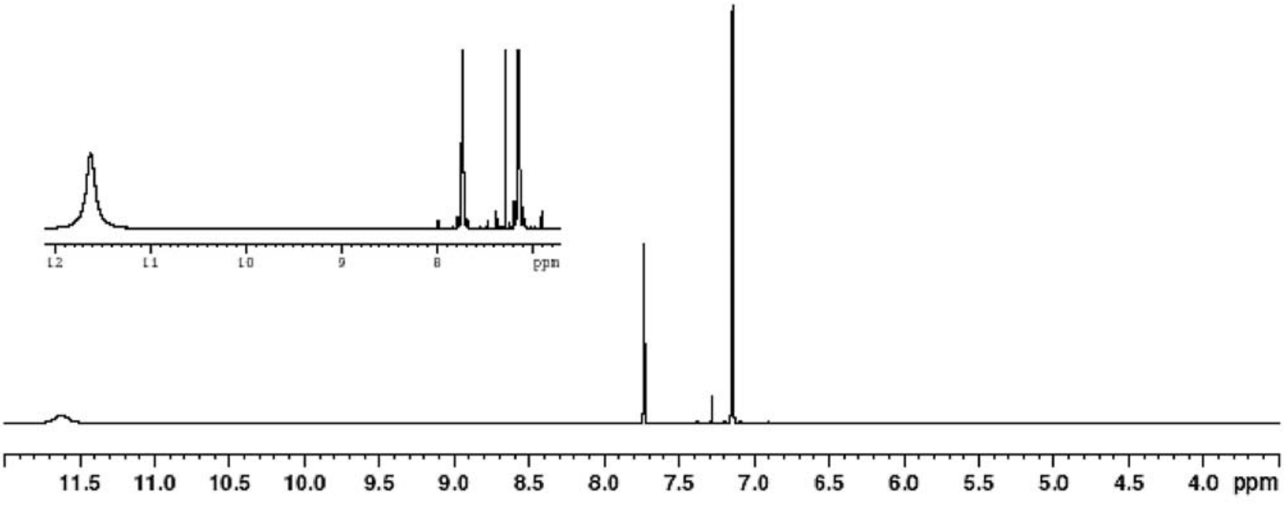


Figure 2. ^{1}H NMR spectrum of imidazole in deuterated chloroform solution (0.1 mol L^{-1}).

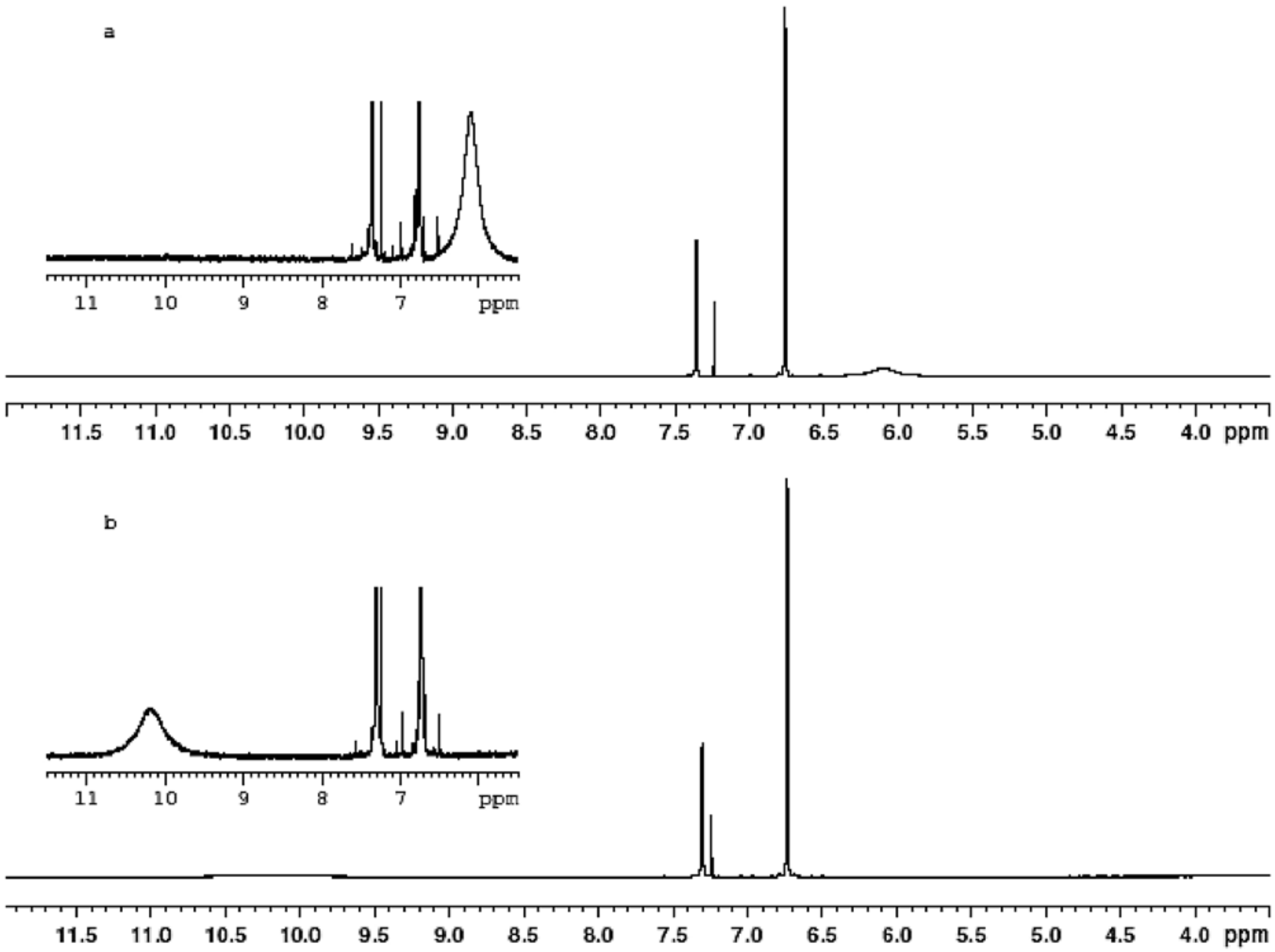
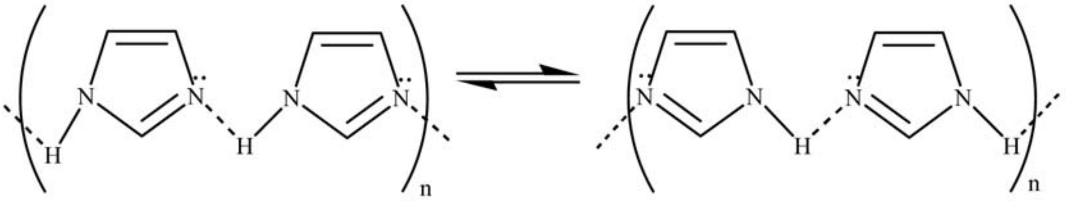


Figure 3. ^{1}H NMR spectrum of 0.1 mol L^{-1} imidazole in acetonitirile-deuterated chloroform solution containing a) 0.1 mol L^{-1} LiBF$_4$ b) 0.1 mol L^{-1} TBABF$_4$



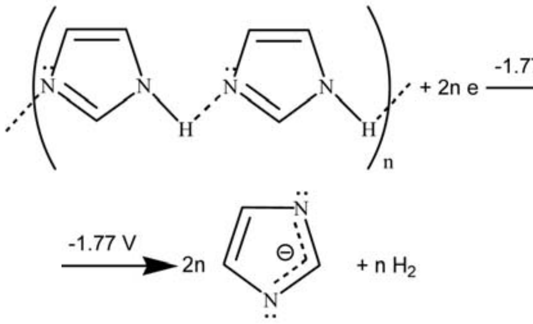
Scheme 2. The tautomerization equilibrium of hydrogen-bonded imidazole cluster.

gen exchange within the cluster. At an intermediate rate of exchange, the N–H proton is partially decoupled, and a broad N–H peak results. The adjacent C–H protons are not split by the N–H proton.[18]

When ^{1}H NMR spectrum of imidazole in chloroform (Figure 2) is compared with that in acetonitrile-chloroform mixture containing TBABF$_4$ (Figure 3b), the chemical shift values are changed from 7.73 ppm, 7.15 ppm, 11.62 ppm to 7.30 ppm, 6.73 ppm, 10.18 ppm. This is due to the fact that intermolecular hydrogen bond formation in chloroform is more pronounced.

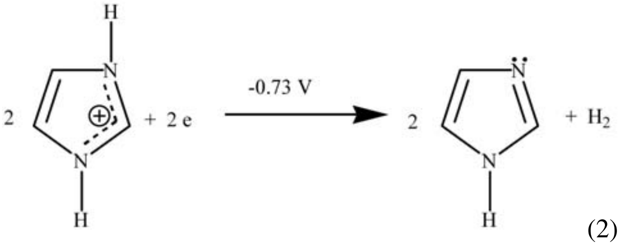
We also performed measurements of the infrared spectra of imidazole in a acetonitrile solution containing TBABF$_4$ and LiBF$_4$. Assignment of characteristic N–H stretching frequencies of imidazole is shown in Figure 4. For comparison, FTIR spectrum of imidazole/acetonitrile in the absence of electrolyte is also given in Figure 4a. Hydrogen-bonded N–H stretching vibration of imidazole obtained in an acetonitrile solution containing TBABF$_4$ corresponds to the peak at about 3359 cm^{-1} (Figure 4b). When LiBF$_4$ is added to imidazole solution instead of TBABF$_4$, the intensity of this peak decreases and the intensities of peaks at about 3626 cm^{-1} and 3546 cm^{-1} increase (Figure 4c). This implies the existence of some interaction of nonbonding electrons with lithium cations. In imidazole solution containing $LiBF_4$, we assigned the peak at 3359 cm^{-1} to N–H stretching, while there is still a peak corresponding to hydrogen-bonded imidazole clusters. The latter signal is weak indicating low population of such clusters. It is interesting that H-bonded entities still exist even in the absence of electrolyte (Figure 4a).

As a result of the formation of hydrogen-bonded oligomers or clusters, the broad electroreduction peak of imidazole is observed in acetonitrile solution containing $TBABF_4$ not $LiBF_4$ (Figures 1a and b, Reaction 1). The broadness of the reduction peak may be due to the involvement of the various chain lengths in such oligomeric structures during electroreduction.



(1)

When increasing amounts of anhydrous HBF_4 were added to 5 mmol L^{-1} imidazole solution, the second reduction peak was observed at –0.73 V vs. Ag/AgCl (Figure 1c, Reaction 2).



(2)

Table 1 shows the calculated heats of formation and total energies of imidazole and its hydrogen-bonded dimer and trimer. The numbers in parenthesis are the corresponding values per unit molecule in dimers and trimers. These values indicate that the stability of the hydrogen-bonded imidazoles increase as the number of intermolecular hydrogen-bonded units increases. The same table lists the calculated hydrogen bond distances in such systems. As seen hydrogen bond distances decrease slightly as the number of hydrogen-bonded units increases. These hydrogen bond length values also support the feasibility of the formation of intermolecular hydrogen bonds in such oligomers.[4,13,19]

Table 2 shows the heats of formation, total energy and hydrogen bond lengths of the hydrogen-bonded dimers and monomer of 2-aminoimidazole (2-ai). The numbers in parenthesis are again the corresponding values per unit molecule in dimers. Inspection of these va-

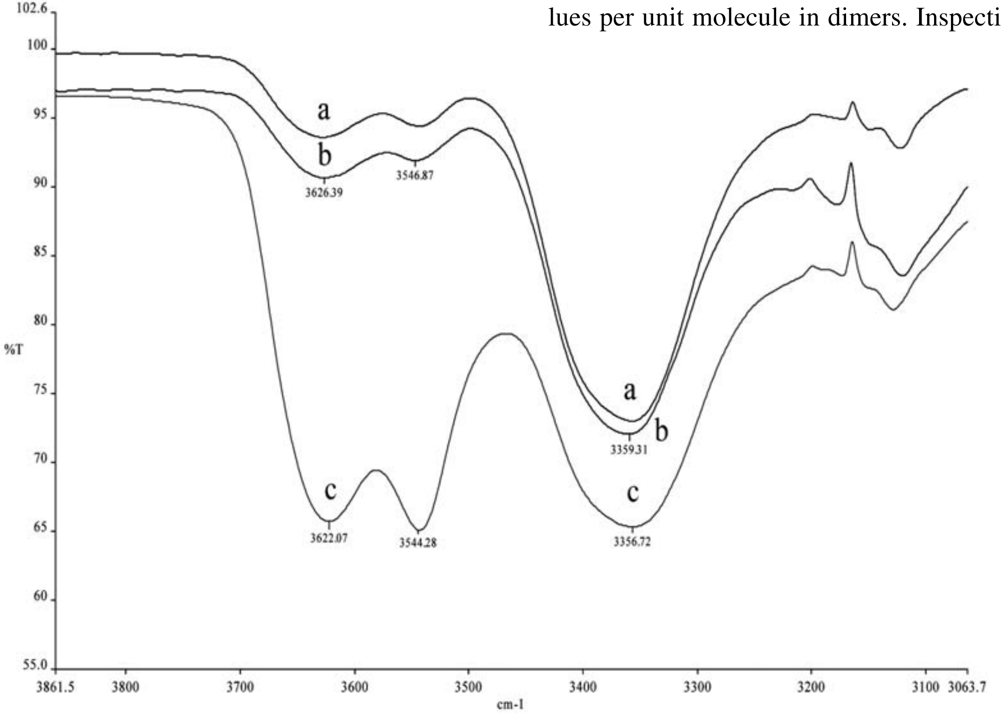
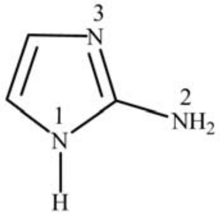


Figure 4. FTIR spectrum of a) acetonitrile solution containing 0.1 mol L^{-1} imidazole; b) acetonitrile/0.1 mol L^{-1} $TBABF_4$ solution containing 0.1 mol L^{-1} imidazole; c) acetonitrile/0.1 mol L^{-1} $LiBF_4$ solution containing 0.1 mol L^{-1} imidazole.

Table 1. Heats of formation and hydrogen bond lengths calculated using AM1 method and total energy (TE) values calculated using ab-initio (STO-3G) method for imidazole and its hydrogen-bonded oligomers.

	ΔH_f (kcal mol^{-1})	**Hydrogen bond length (Å)**	***TE* (kcal mol^{-1})**
Monomer	50.726	—–	–139299.58
Dimer	98.431 (49.216)	2.4885	–278609.78 (–139304.89)
Trimer	145,55 (48.517)	2.4820, 2.4824	–417923.06 (–139307.69)

lues leads to the prediction that the dimers are most probably formed as a result of the intermolecular hydrogen bonding between 1 and 2 positions in 2-ai since ΔH_f and TE values are minimal in such dimers (Formula 2). Heats of formation and hydrogen bond lengths values for intramolecular hydrogen-bonded 2-ai on 1 and 2 position are also given in Table 2. The number in parenthesis is the corresponding value for two moles intramolecular hydrogen-bonded 2-ai.

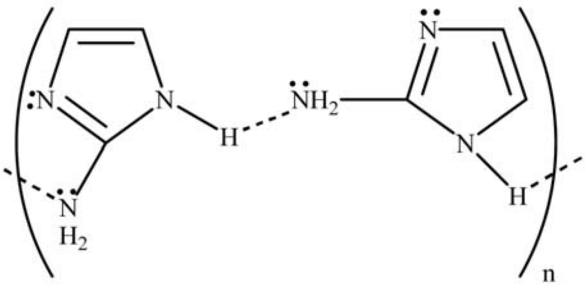


Formula 2. The structure of 2-aminoimidazole.

Table 2. Heats of formation and hydrogen bond lengths calculated using AM1 method and total energy values calculated using ab initio (STO-3G) method for intermolecular hydrogen-bonded 2-ai dimers.

	ΔH_f (kcal mol^{-1})	**Hydrogen bond length (Å)**	***TE* (kcal mol^{-1})**
Intermolecular hydrogen bonded dimer			
1–3 position	102.81 (51.405)	2.5593	–346788.91
1–2 position	102.46 (51.230)	2.7943	–346796.59
Intramolecular hydrogen bonded monomer			
1 and 2 position	52.469	2.7577	–173389.28 (–346778.56)

The latter values indicate that the following type of intermolecular hydrogen bond formation is preferred for this compound (Scheme 3).



Scheme 3. Hydrogen-bonded 2-aminoimidazole clusters.

Table 3 lists the heats of formation and total (bonding) energies of monomers of 2-ai and its dimers and trimers formed by hydrogen bonding between 1 and 2 positions of neighbouring rings. The numbers in parenthesis are again the corresponding values per unit molecule in dimers and trimers. The stability increase of the hydrogen-bonded oligomers is also evident here as the number of hydrogen-bonded units increases. The hydrogen bond distances also indicate the feasibility of hydrogen bond formation.[4,13,19]

Table 3. Heats of formation and hydrogen bond lengths calculated using AM1 method and total energy (TE) values calculated using ab-initio (STO-3G) method for 2-ai and its hydrogen-bonded oligomers.

	ΔH_f (kcal mol^{-1})	**Hydrogen bond length (Å)**	***TE* (kcal mol^{-1})**
Monomer	56.01	—	–173383.31
Dimer	102.5 (51.23)	2.7943	–346789.60 (–173394.80)
Trimer	148.9 (49.63)	2.8123, 2.6911	–520194.90 (–173398.30)

Figure 5 shows ^{1}H NMR spectra of 2-ai in acetonitrile-deuterated chloroform containing $LiBF_4$ and $TBABF_4$ respectively. Because of tautomerization a singlet peak, which belong to two equivalent C–H protons in the imidazole ring, is recorded at 6.29 ppm for 2-ai with $LiBF_4$ (Figure 3a) and at 6.19 ppm with $TBABF_4$ (Figure 3b). The broad $–NH_2$ peaks are observed at 4.32 ppm with $LiBF_4$ and at 4.13 ppm with $TBABF_4$. N–H proton on the nitrogen in the imidazole ring gives rise to a broad peak at 4.64 ppm and 5.34 ppm in acetonitrile containing $LiBF_4$ and $TBABF_4$ respectively. In contrast to imidazole, the peak belonging to N–H proton in the imidazole ring for 2-ai is not shifted to the lower fields as much as was the case in imidazole with $TBABF_4$. This is an evidence for the fact that nonbonding electrons on the nitrogen center are not participating in hydrogen bonding. In other words, the hydrogen bond is primarily

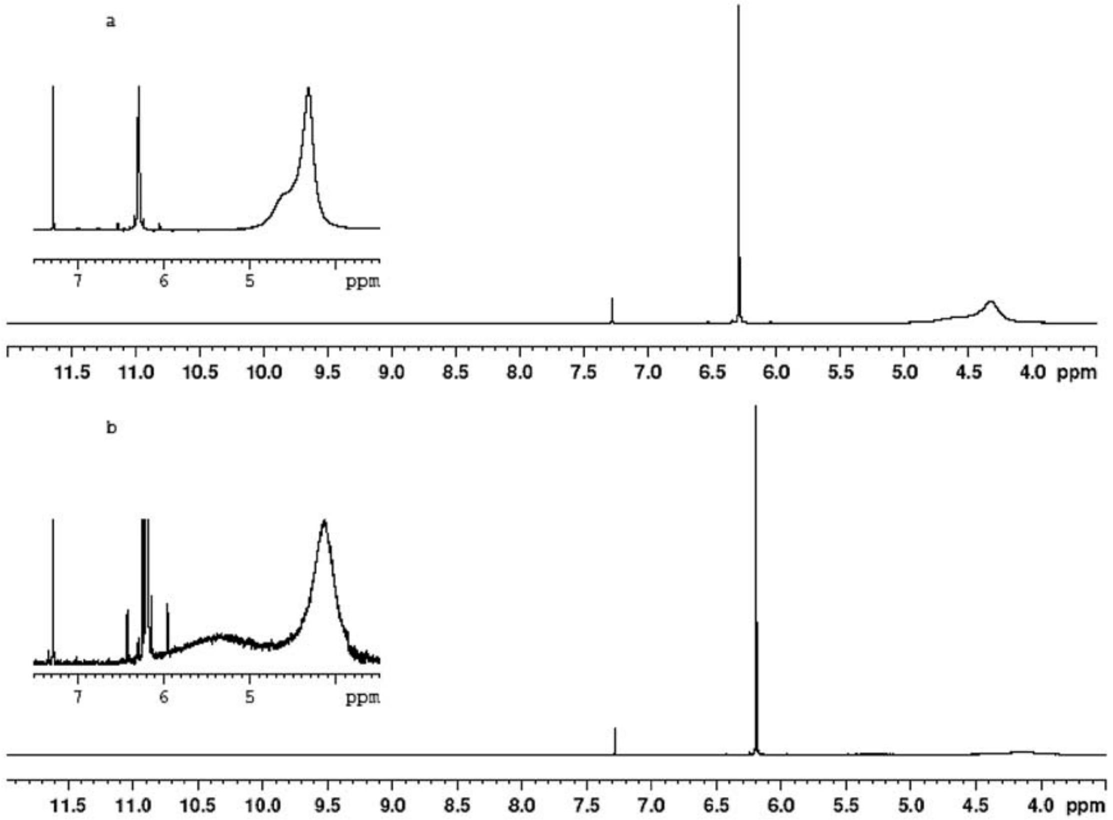


Figure 5. ^{1}H NMR spectrum of 0.1 mol L^{-1} 2-ai in acetonitirile-deuterated chloroform solution containing a) 0.1 mol L^{-1} LiBF$_4$ b) 0.1 mol L^{-1} TBABF$_4$.

constructed between N–H and –NH$_2$ centers of the neighboring molecules. The fact that –NH$_2$ peak is not a sharp peak as is the case in the aniline,[17] supports the involvement of –NH$_2$ protons in hydrogen bond formation with the N–H proton, which also takes part in a tautomeric equilibrium.

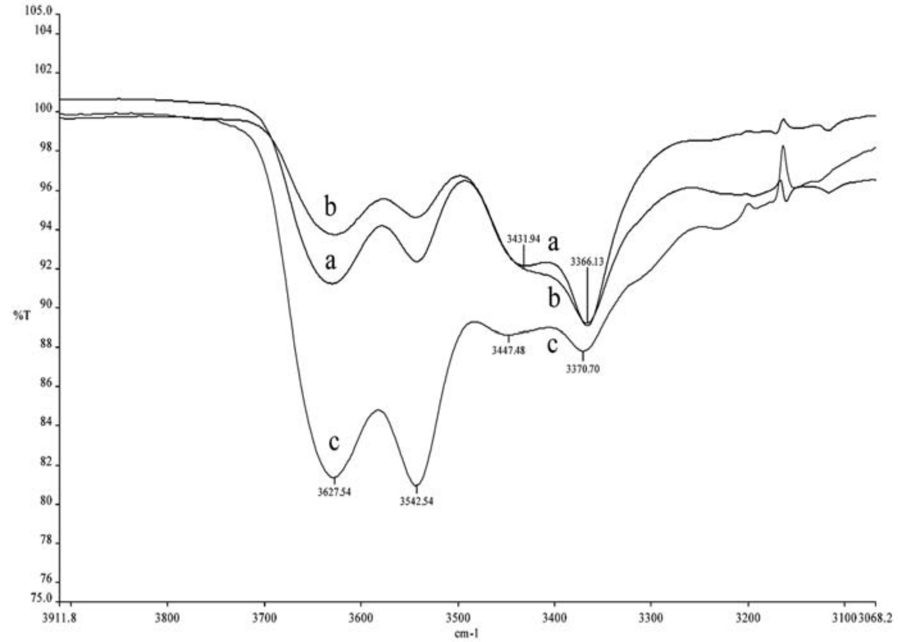
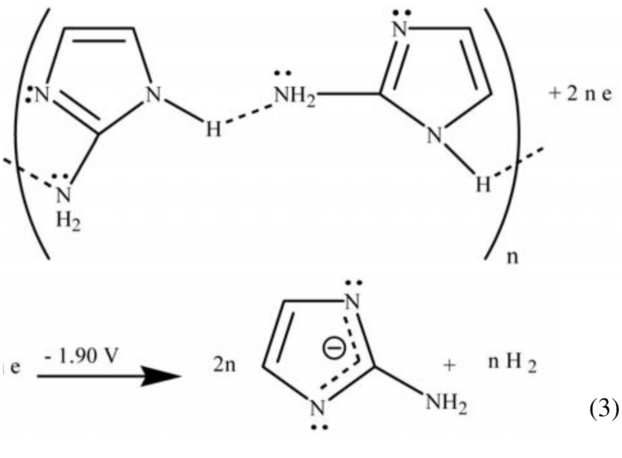


Figure 6. FTIR spectrum of a) acetonitrile solution containing 0.05 mol L^{-1} 2-ai; b) acetonitrile/0.2 mol L^{-1} TBABF$_4$ solution containing 0.05 mol L^{-1} 2-ai; c) acetonitrile/0.1 mol L^{-1} LiBF$_4$ solution containing 0.05 mol L^{-1} 2-ai.

Figure 6 shows the infrared spectra of 2-ai in an acetonitrile solution containing $TBABF_4$ and $LiBF_4$. Assignments of characteristic N–H stretching frequencies are also shown on figures. Hydrogen-bonded N–H stretching vibration of 2-ai in an acetonitrile solution with and without $TBABF_4$ corresponds to the peak at about 3366 cm^{-1} (Figures 6 a and b). When $LiBF_4$ is added to imidazole solution instead of $TBABF_4$, the intensity of this peak decrease and the intensity of peaks at about 3627 cm^{-1} and 3542 cm^{-1} increase similar to that of imidazole (Figure 6 c). In addition, hydrogen-bonded N–H stretching vibration of $–NH_2$ groups of 2-ai in a solution containing $TBABF_4$ corresponds to the peak at about 3432 cm^{-1} (Figure 6b). This broad peak is blue-shifted to 3447 cm^{-1} due to interaction of nonbonding electrons of $–NH_2$ groups with lithium cations (Figure 6 c). In other words, the hydrogen bond is primarily constructed between N–H and $–NH_2$ centers of the neighbouring molecules. These observations imply the existence of some interaction of nonbonding electrons of 2-ai with lithium cations similar to that of imidazole. There is still a peak at about 3371 cm^{-1} corresponding to hydrogen-bonded imidazole clusters in 2-ai solution containing $LiBF_4$. This signal is again too weak indicating low population of such clusters. H-bonded entities still exist even in the absence of electrolyte (Figure 6a) as was the case in imidazole.

Theoretical predictions and ^{1}H NMR and FTIR evidences are supported by the electroreduction behaviour of 2-ai. The electroreduction of 2-ai is recorded at a peak potential of –1.90 V vs. Ag/AgCl in acetonitrile/0.1 mol L^{-1} $TBABF_4$ as seen in the cyclic voltammogram (Figure 7a.) (Reaction 3). There is no reverse reduction peak. Again no reduction peak was observed when 0.1 mol L^{-1} $LiClO_4$ was used as supporting electrolyte as was the case with imidazole.



(3)

When increasing amounts of anhydrous HBF_4 (up to 2 mmol L^{-1}) were added to 5 mmol L^{-1} 2-ai solution, the second reduction peak was observed at –1.00 V vs. Ag/AgCl (Figures 7 b, c, d, e and f). The cyclic voltammogram of aniline in the same medium containing HBF_4 shows one reduction peak at a peak potential of –0.85 V vs. Ag/AgCl.[13,20] This reduction belongs to the catalytic reduction of protons through the protonated amine group bonded to the aromatic ring (Reaction 4).

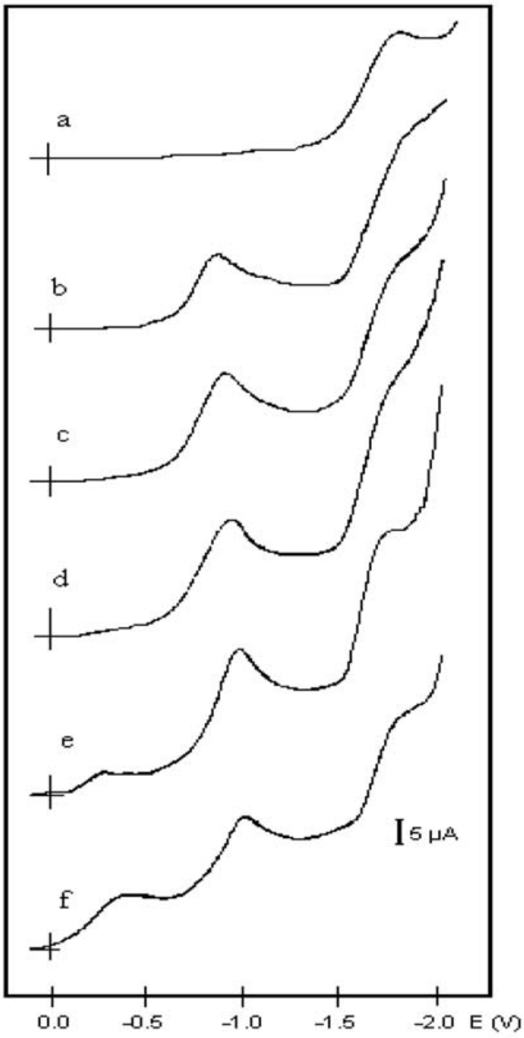
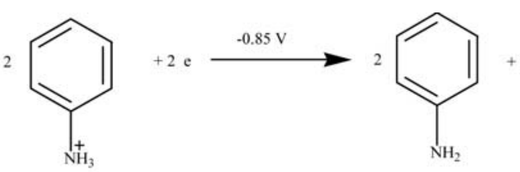
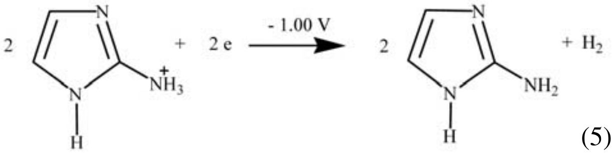


Figure 7. The voltammograms of acetonitrile/0.1 mol L^{-1} $TBABF_4$ solution containing a) 5 mmol L^{-1} 2-aminoimidazole (2-ai) b) 5 mmol L^{-1} 2-ai + 2 mmol L^{-1} HBF_4 c) 5 mmol L^{-1} 2-ai + 2.5 mmol L^{-1} HBF_4 d) 5 mmol L^{-1} 2-ai + 3 mmol L^{-1} HBF_4 e) 5 mmol L^{-1} 2-ai + 3.5 mmol L^{-1} HBF_4 f) 5 mmol L^{-1} 2 ai + 5 mmol L^{-1} HBF_4. Scan rate: 100 mV sec^{-1}.



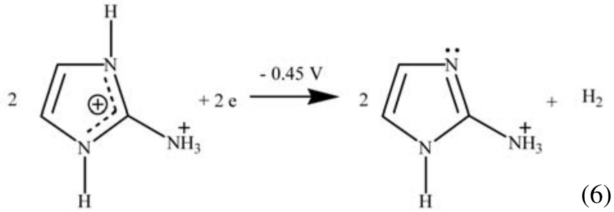
(4)

Therefore the reduction peak observed for 2-ai at –1.00 V vs. Ag/AgCl should be due to following reduction process (Reaction 5).



(5)

A third reduction peak at –0.45 V vs. Ag/AgCl was recorded for 2-ai, belonging to the electroreduction of the following doubly protonated species upon the addition of excess amount of acid (Figures 7 e, f, Reaction 6).



(6)

The appearance of the reduction peak at –1.00 V vs. Ag/AgCl first upon addition of acid indicates that the nitrogen center of the –NH$_2$ group is more basic than the nitrogen center in the imidazole ring because of the tautomeric equilibrium, and therefore is protonated before the ring nitrogen.

The reduction of N center in the imidazole ring of 2-ai is shifted by 280 mV from –0.73 V to –0.45 V vs. Ag/AgCl compared to that of imidazole. This is apparently because of the close proximity of two positively charged centers in doubly protonated 2-ai.

4. Conclusions

It can be concluded that the intermolecular hydrogen bonds enable the formation of electroreducible imidazole clusters in neutral medium. The intermolecular hydrogen bonds are formed between N and N–H centers of the neighboring rings in imidazole in acetonitrile containing tetrabutylammonium tetrafluoroborate. For 2-aminoimidazole, on the contrary, the N–H and –NH$_2$ centers of the neighboring molecules are primarily utilized for the formation of clusters in the same medium. The addition of HBF$_4$ protonates the N centers of the ring in imidazole where, as in 2- amino imidazole, –NH$_2$ centers are protonated before the N centers of the ring are protonated. The protonated species are reduced at much more positive potentials giving rise to additional reduction peaks. The ^{1}H NMR data also suggest that tautomeric equilibria exist for these compounds.

5. Acknowledgements

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6. References

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Povzetek

Študirali smo elektroredukcijo imidazola in 2-aminoimidazola na Pt elektrodi v acetonitrilu, ki je vseboval tetrabutilamonijev tetrafluoroborat, brez in v prisotnosti HBF$_4$. Narejena je bila primerjava vpliva litijevih in tetrabutilamonijevih ionov na elektroredukcijo in rezultate FTIR ter ^{1}H NMR meritev. Z uporabo teoretičnih izračunov smo poskušali pojasniti rezultate raziskav s tvorbo inter- in intramolekularnih vodikovih vezi. Rezultati raziskav elektroredukcije v acetonitrilu, ki vsebuje tudi tetrabutilamonijev tetrafluoroborat, kažejo na obstoj skupkov povezanih z vodikovo vezjo.