J Mol Model (2011) 17:2687–2692
DOI 10.1007/s00894-011-0955-1

ORIGINAL PAPER

Computational study of proton and methyl cation affinities of imidazole-based highly energetic ionic liquids

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Received: 1 October 2010 / Accepted: 3 January 2011 / Published online: 29 January 2011

Abstract The present study deals with the evaluation of gas phase proton and methyl cation affinities for alkyl- and nitrosubstituted imidazoles using DFT (B3LYP)/6-31+G(d) and MP2 methods in the Gaussian 03 software package. The extent of charge delocalization of these cations is correlated with proton affinity. The study reveals that weakly electron-donating alkyl groups at position 1 of the imidazole enhance its proton affinity, which also increases with increasing alkyl chain length. This is expected to result in an increased tendency to form salts. In contrast, the presence of strongly electron-withdrawing nitro groups lowers proton affinity, which decreases as the number of nitro groups on the ring increases. The same trend is observed for the methyl cation affinity, but to a lower degree. These trends in the proton and methyl cation affinities were analyzed to study the effects of these substituents on the basicity of the energetic imidazole moieties and their tendency to form salts. This, in turn, should aid searches for better highly energetic ionic liquids. In addition, calculations performed on different isomers of mono and dinitroimidazoles show that 5-nitro-1H-imidazole and 2,4-dinitro-1H-imidazole are more stable than the other isomers. Amongst the many nitro derivatives of imidazoles considered in the present study, cations resulting from these two would be the best choice for creating highly energetic ionic liquids when coupled with appropriate energetic anions.

Keywords Energetic ionic liquids · Imidazolium ion · Proton affinity · Methyl cation affinity · Salt formation tendency

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Introduction

Ionic liquids are low-melting salts that consist entirely of ions and are liquids at room temperature; or more specifically, they have melting points that are below 100 °C [1]. They are also thermally stable and have negligible vapor pressure. Thus, they have the potential to combine the useful characteristics of solid salt systems with the handling advantages of liquid systems [2]. Ionic liquids generally consist of bulky organic cations such as the 1-butyl-3-methylimidazolium ion (BMIM) coupled to an inorganic ion such as a halide, nitrate, perchlorate, dinitramide, etc. As they consist of two components, a cation and an anion, ionic liquids can be tailored to possess a particular required set of properties, and it is also possible to design new energetic ionic liquids [3]. A few important characteristics of ionic liquids that should be kept in mind when designing a new series are: a low melting point (usually less than 100 °C), a high thermal stability, a high decomposition temperature, a high liquidus range (often >200 °C), and almost negligible vapor pressure [4, 5].

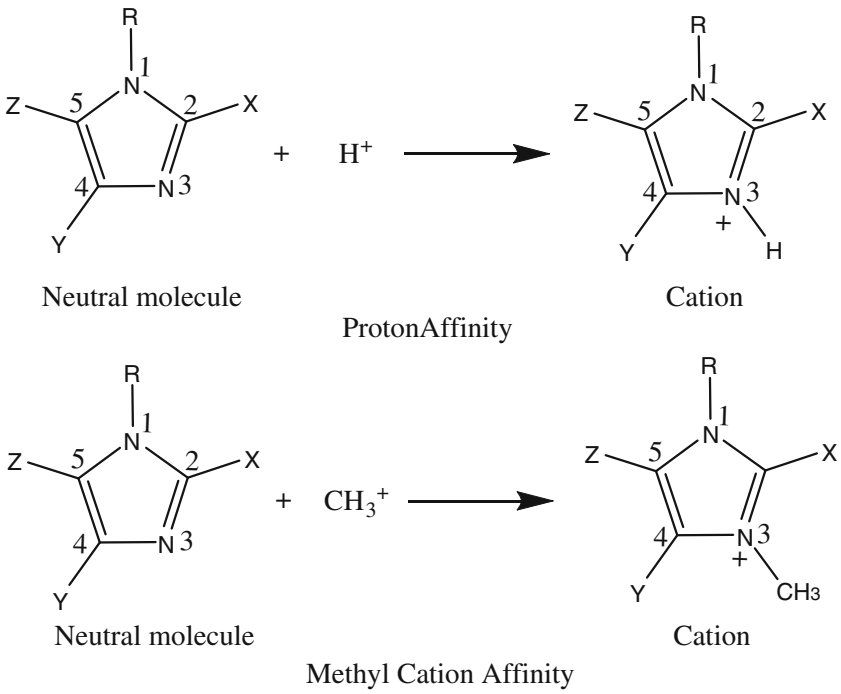
Highly energetic materials are capable of releasing large amounts of energy on decomposition, so they are critical components of explosives and propellants [6]. Their enhanced dissolving powers, densities and compatibilities with a wide range of propellant ingredients make ionic liquids a very attractive class of materials for advanced state-of-the-art propulsion systems [7]. They can also be used as safe explosives, as they are environmentally safe and show reduced sensitivity to external stimuli such as impact, friction, shock, etc. [8]. Recently, N-heterocycles have drawn great attention because it is usually possible to split off the N atoms present in these molecules in the form of N_2, which releases an energy equivalent of 942 kJ mol^{-1}.

Such molecules with many nitrogen atoms yield relatively high energies upon the release of this nitrogen [9, 10]. The energy content of an ionic liquid can also be enhanced by substituting its components with energy-enhancing groups such as nitro, cyano, and azido groups [11]. Due to their strong electrostatic interactions, inorganic salts are usually solids at room temperature. In the case of ionic liquids, this electrostatic interaction must be reduced in order to make them liquid at room temperature. This can be achieved by delocalizing the charge on the anion or shielding the charge on the cation. Such an approach forms the basis for the design of ionic liquids with desired properties through anion and cation tuning. Recently, Izgorodina et al. [12] proposed that proton affinity could be used as a criterion to gauge the extent of charge delocalization in the molecule. In the present work, computational studies were performed at the DFT (B3LYP)/6-31+G(d) and MP2 levels to calculate the proton affinity (H atom at position 3) of an imidazole ring containing various alkyl and energy-enhancing nitro groups as constituents. In addition to the proton affinity, the methyl cation affinity of the imidazole was calculated, and the results are compared below. The proton and methyl cation affinities are defined as the negative of the enthalpy change in each of the reactions shown in Scheme 1. Four different series of compounds were studied in detail (see Scheme 1, where X, Y and Z are different substituent groups attached to imidazole moieties). We envisage that this study may aid in the design of imidazolium-based highly energetic ionic liquids.

Computational methods

Electronic structure calculations were performed using the Gaussian 03 software package. Electronic energies, zero point energies and proton affinities were calculated at the DFT/B3LYP level of theory using the 6-31+G(d) basis set which incorporated diffuse and polarized basis sets to a small extent. Møller–Plesset perturbation (MP2) was also employed in a few cases to check the accuracy of the data computed at DFT/B3LYP method. The proton affinity was calculated as the negative of the enthalpy change in the gas phase reaction (real or hypothetical) between a proton (or, more correctly, a "hydron") and the chemical species concerned, which was usually an

Scheme 1 Series of imidazolium-based compounds studied



(i) X and Y = H, Z = NO_2 (Mononitroimidazole)

(ii) X and Y = NO_2, Z = H (Dinitroimidazole)

(iii) X , Y and Z = NO_2 (Trinitroimidazole)

(iv) R = Alkyl group (methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and t-butyl)

Table 1 Electronic energies, zero-point energies and proton affinities ($-\Delta H_{298}$) for imidazole and alkyl-substituted imidazoles. Values are given in kcal mol^{-1}

Molecule	B3LYP/6-31+G(d)			MP2/6-31+G(d)		
	ΔE_{elec}	ΔZPE	ΔH_{298}	ΔE_{elec}	ΔZPE	ΔH_{298}
1H-imidazole	231.74	−8.87	222.86 (225.33)*	228.51	−8.96	219.57
1-Methylimidazole	236.42	−8.73	227.64 (229.34)*	240.87	−8.79	224.35
1-Ethylimidazole	237.62	−8.79	228.79	234.54	−8.75	225.75
1-*n*-Propylimidazole	238.74	−8.68	229.97	234.46	−8.68	225.69
1-Isopropylimidazole	239.80	−8.72	231.05	236.04	−8.79	227.25
1-*n*-Butylimidazole	239.12	−8.62	230.41	234.79	−8.67	226.04
1-Isobutylimidazole	239.16	−8.68	230.40	235.39	−8.71	226.61
1-*t*-Butylimidazole	241.91	−8.68	232.60 (235.89)*	237.95	−8.75	228.61

* The experimental proton affinity (PA) values provided by Hunter and Lias [17]

electrically neutral species, in order to give the conjugate acid of that species [13]. Thus, it is the energy released in the following reactions:

$$B + H^+ \rightarrow BH^+ \text{ (proton affinity)} \quad (1)$$

$$B + CH_3{}^+ \rightarrow BCH_3{}^+ \text{ (methyl cation affinity)}. \quad (2)$$

Thus proton affinity (PA) in the case of the neutral species in Eq. 1 is given by $[E(B)+E(H^+) - E(BH^+)]$ [14], and the methyl cation affinity (MCA) for Eq. 2 is given by $[E(B)+E(CH_3{}^+) - E(BCH_3{}^+)]$. The H^+ contribution at 298 K is 5/2 *RT* or 1.48 kcal mol^{-1} [15], which is only a small contribution and so was not included in our calculations. The proton affinity and the methyl cation affinity is determined as $-\Delta H_{298}$ for the respective species calculated via reactions (1) and (2), respectively. The absolute enthalpies of the isomers of mono and dinitroimidazoles are calculated at the G2 level of theory, and the heats of formation are evaluated using the atomization method [16].

Results and discussion

Protonated ions (proton affinity)

The proton affinities of imidazole and imidazoles containing alkyl substituents with various chain lengths are listed in Table 1. The results shown in Table 1 indicate that the data obtained via DFT and MP2 for ΔE_{elec}, ΔZPE and ΔH_{298} are almost the same; the variation between the results from DFT and MP2 is the range of 2–4 kcal mol^{-1}.

The results in Table 1 further reveal that when alkyl groups are inserted at position 1 of the imidazole ring, increasing the chain length of the alkyl group increases the proton affinity from 224.35 to 228.61 kcal mol^{-1} (MP2 level). This increase may be attributed to the fact that alkyl groups are weakly electron donating, so they add electron density to the imidazole ring. This enhances ring basicity, resulting in a small increase in the proton affinities of these alkyl-substituted imidazoles. The data show that the presence of branching in the alkyl chain causes a very slight increase in the proton affinity, as is evident from the cases of 1-*n*-propylimidazole (225.69 kcal mol^{-1}) and 1-isopropylimidazole (227.25 kcal mol^{-1}). Similarly, for butyl-substituted imidazole, the *n*-butyl and isobutyl chains have almost similar values of 226.04 and 226.61 kcal mol^{-1}, respectively, while the *t*-butyl chain has a slightly larger value (228.61 kcal mol^{-1}). Thus, it may be concluded that increasing the chain length of any alkyl group on the ring increases the proton affinity of the imidazole, which may in turn lead to a greater tendency for salt formation. Furthermore, the present study reveals that alkyl group branching does not have a significant effect on the proton affinity. In a few cases the data have been compared with the experimental values provided by

Table 2 Total energies (E_0, in Hartrees) of mono- and dinitroimidazole isomers at the DFT and MP2 levels

Molecule	B3LYP/6-31+G(d)	MP2/6-31+G(d)
2-Nitro-1H-imidazole	−430.7327749	−429.5547151
4-Nitro-1H-imidazole	−430.7349041	−429.5562699
5-Nitro-1H-imidazole	−430.7362301	−429.5553766
2,4-Dinitro-1H-imidazole	−635.2329073	−633.5686351
2,5-Dinitro-1H-imidazole	−635.232013	−633.5681196
4,5-Dinitro-1H-imidazole	−635.2238274	−633.5627639

Table 3 Heats of formation ($\Delta_f H^0$) of mono- and dinitroimidazole isomers at the G2 level

Molecule	$\Delta_f H^0$ (kcal/mol)
2-Nitro-1H-imidazole	28.73
4-Nitro-1H-imidazole	27.10
5-Nitro-1H-imidazole	26.98
2,4-Dinitro-1H-imidazole	26.98
2,5-Dinitro-1H-imidazole	27.91
4,5-Dinitro-1H-imidazole	31.94

Table 4 Electronic energies, zero-point energies and proton affinities ($-\Delta H_{298}$) for 5-nitro-1H-imidazole and alkyl-substituted nitroimidazoles. Values shown are in kcal mol^{-1}

Molecule	B3LYP/6-31+G(d)			MP2/6-31+G(d)		
	ΔE_{elec}	ΔZPE	ΔH_{298}	ΔE_{elec}	ΔZPE	ΔH_{298}
5-Nitro-1H-imidazole	212.13	−8.38	203.67	210.75	−8.52	202.21
1-Methyl-5-nitroimidazole	217.58	−8.31	208.85 (213.98)*	215.72	−8.39	207.28
1-Ethyl-5-nitroimidazole	219.99	−8.24	211.66	218.27	−8.37	209.29
1-*n*-Propyl-5-nitroimidazole	219.52	−8.27	211.14	218.10	−8.32	209.70
1-Isopropyl-5-nitroimidazole	221.21	−8.19	212.89	219.31	−8.38	210.88
1-*n*-Butyl-5-nitroimidazole	218.89	−8.31	210.48	218.67	−8.29	210.28
1-Isobutyl-5-nitroimidazole	218.71	−8.32	210.34	218.65	−8.32	210.25
1-*t*-Butyl-5-nitroimidazole**	—	—	—	—	—	—

* The experimental proton affinity value as given by Hunter and Lias [17]

** 1-*t*-Butyl-5-nitroimidazole was not included because of its hindered structure

Hunter and Lias [17], as shown in Table 1. These two data sets show close agreement.

The analysis of nitro derivatives of 1H-imidazole reveals that three mononitro and three dinitro derivatives but only one trinitro derivative are possible. The results presented in Table 2 show that, among all three of the mononitroimidazoles, 5-nitro-1H-imidazole is the most energetically stable, as the total energy calculated at the DFT level for this mononitroimidazole was found to be the lowest. In contrast to this, the values calculated at the MP2 level and recorded in Table 2 show that 4-nitro-1H-imidazole is the most energetically stable. However, a comparison of the heat of formation values evaluated at the G2 level during the present study using the atomization method, as shown in Table 3, indicates that 5-nitro-1H-imidazole exhibits a lower value of 26.98 kcal mol^{-1} than that for 4-nitro-1H-imidazole, 27.10 kcal mol^{-1}, thus implying that 5-nitro-1H-imidazole is more energetically stable. These calculated values of heats of formation are in good agreement with the values calculated by Xinfang et al. [18] using a higher level of basis set (B3LYP/6-311 G(d,p)). This is further substantiated by another study performed at the MNDO PM3 level by Kolaric et al. [19], who showed that 5-nitro-1H-imidazole is more stable than its counterpart 4-nitro-1H-imidazole. At the same time, nitro substitution at position 5 on the imidazole ring is known to be more favorable when the ring already contains an alkyl group at position 1 [20]. Thus, 5-nitro-1H-imidazole is the preferred mononitroimidazole, and the change in its proton affinity with the length of the alkyl group at position 1 was calculated. The same criterion was applied to the dinitroimidazole isomers. Calculations performed on the three dinitroimidazole isomers (2,4-, 2,5- and 4,5-) at the DFT and MP2 levels show that, among the three dinitro isomers, the first (2,4-) is the most thermodynamically stable [18]. Thus, 2,4-dinitro-1H-imidazole was selected as the representative for the dinitroimidazole series in further alkyl group substitutions. The proton affinity results for 5-nitro-1H-imidazole, 2,4-dinitro-1H-imidazole and their alkyl-substituted derivatives are recorded in Tables 4 and 5, respectively.

The results shown in Table 4 indicate that the proton affinity of 5-nitro-1H-imidazole is 202.21 kcal mol^{-1} (MP2 value), which is lower than that of the simple 1-alkyl-substituted imidazoles (Table 1). This is probably due to the electron-withdrawing nature of the nitro group. Similarly, when alkyl groups of various chain lengths are added to 5-nitro-1H-imidazole, the proton affinity is enhanced from 207.28 kcal mol^{-1} (1-methyl-5-nitroimidazole) to 210.25 kcal mol^{-1} (1-isobutyl-5-nitroimidazole). The experimental value of the proton affinity (PA) for 1-methyl-5-nitroimidazole is given by Hunter and Lias [17] as 213.98 kcal mol^{-1}, which is in agreement with our calculated value of 207.28 kcal mol^{-1}, obtained at the MP2 level. An increase in proton affinity values (of about 10 to 11 kcal mol^{-1}) is also observed in the case of alkylated dinitro- and trinitroimidazoles as compared to the 2,4-dinitro-1H-imidazole and 2,4,5-trinitro-1H-imidazole, as shown in Tables 5 and 6, respectively. This calculation shows that the proton affinities of the nitro derivatives are lower than those seen when the imidazoles contain alkyl group substituents, because nitro groups supposedly have a stronger effect than

Table 5 Electronic energies, zero-point energies and proton affinities ($-\Delta H_{298}$) for 2,4-dinitroimidazoles and alkyl-substituted dinitroimidazoles. Values are in kcal mol^{-1}

Molecule	B3LYP/6-31+G(d)		
	ΔE_{elec}	ΔZPE	ΔH_{298}
2,4-Dinitro-1H-imidazole	194.89	−7.97	186.78
1-Methyl-2,4-dinitroimidazole	201.54	−7.88	193.48
1-Ethyl-2,4-dinitroimidazole	203.31	−7.91	195.26
1-*n*-Propyl-2,4-dinitroimidazole	205.25	−7.89	197.23
1-Isopropyl-2,4-dinitroimidazole	205.98	−7.76	198.03
1-*n*-Butyl-2,4-dinitroimidazole	205.29	−7.79	197.31
1-Isobutyl-2,4-dinitroimidazole	205.46	−7.86	197.44
1-*t*-Butyl-2,4-dinitroimidazole *	—	—	—

* 1-*t*-Butyl-2,4-dinitroimidazole was not included because of its hindered structure

Table 6 Electronic energies, zero-point energies and proton affinities ($-\Delta H_{298}$) for alkyl-substituted trinitroimidazoles. Values are in kcal mol^{-1}

Molecule	B3LYP/6-31+G(d)		
	ΔE_{elec}	ΔZPE	ΔH_{298}
2,4,5-Trinitro-1H-imidazole	182.30	−7.5	174.61
1-Methyl-2,4,5-trinitroimidazole	190.33	−7.5	182.54
1-Ethyl-2,4,5-trinitroimidazole	192.82	−7.6	185.04
1-*n*-Propyl-2,4,5-trinitroimidazole	194.37	−7.6	186.61
1-Isopropyl-2,4,5-trinitroimidazole	195.29	−7.6	187.52
1-*n*-Butyl-2,4,5-trinitroimidazole *	—	—	—
1-Isobutyl-2,4,5-trinitroimidazole	193.03	−7.8	185.17
1-*t*-Butyl-2,4,5-trinitroimidazole *	—	—	—

* 1-*n*-Butyl-2,4,5-trinitroimidazole and 1-*t*-butyl-2,4,5-trinitroimidazole could not be optimized, possibly because of hindered structures

alkyl groups [21]. This trend for a decrease in proton affinity values continues as we increase the number of nitro groups on the alkylated imidazoles. This is evident from the proton affinity value of 210.25 kcal mol^{-1} for 1-isobutyl-5-nitroimidazole (Table 4), which drops to 197.44 kcal mol^{-1} for 1-isobutyl-2,4-dinitroimidazole (Table 5), and ultimately to 185.17 kcal mol^{-1} for 1-isobutyl-2,4,5-trinitroimidazloe at the DFT level (Table 6). This effect can be assigned to the fact that the nitro group causes greater charge delocalization of the imidazolium ion, resulting in a decrease in the basicity of the imidazole ring, ultimately leading to a decrease in the proton affinity. A lower proton affinity results in a lower tendency to form salts. The decreased basicity of the imidazole precursor can be overcome by using a protonating or alkylating agent of suitable strength in order to encourage salt formation [21], and the presence of nitro groups at positions 2, 4 and 5 on the imidazole ring result in an increase in the energy content.

During the present study we always encountered a problem when optimizing species containing a highly branched bulky alkyl chain. For example, in the cases of 1-*t*-butyl-5-nitroimidazole, 1-*t*-butyl-2,4-dinitroimidazole, 1-butyl-2,4,5-trinitroimidazole and 1-*t*-butyl-2,4,5-trinitroimidazole, the hydrogens of the alkyl group are very close to the oxygen of the nitro group, which in turn would be expected to yield a strong interaction. The optimization of such molecules could not be achieved at the DFT level. Since branching affects the proton affinity values only slightly, as noted for the alkyl-substituted imidazoles, we can guess that adding branched bulky alkyl groups such as *t*-butyl as substituents would not lead to a significant increase in the proton affinity.

Methylated ions (methyl cation affinity)

The methyl cation affinities of 1-ethylimidazole and its nitro-substituted derivatives were calculated at the DFT and MP2 levels of theory, and the results are listed in Table 7. In contrast to the proton affinity, we did not vary the chain length so that we could concentrate on the effects of nitro and ethyl group substitution on the methyl cation affinity. The values listed in Table 7 show that the methyl cation affinities found for all of the cases studied during the course of the present investigation were lower than the proton affinities of the analogous imidazole derivatives. The results shown in Table 7 include a value of 132.52 kcal mol^{-1} that was obtained at the MP2 level of theory for 1-ethylimidazole, which is in good agrreement with the value of 131.45 kcal mol^{-1} determined for 1-methylimidazole by Wei et al. [22]. Since the electron-donating capabilities of the ethyl and methyl groups are almost the same, the values may be compared with an acceptable degree of confidence to our calculated values for the methyl cation affinities of other species shown in Table 7. As the number of nitro group substituents increases, the methyl cation affinity drops. The lowest value of 89.4 kcal mol^{-1} is obtained for 1-ethyl-2,4,5-trinitroimidazole at the MP2 level. Thus, we can predict that this cation may form a low-melting highly energetic salt [23] that could be used in explosive and propellant formulations. We may further conclude that methyl group substitution at position 3 of the imidazole ring results in more delocalized imidazolium cations. Also, the imidazole ring with a methyl group at position 3 was found to be thermally stable than its protonated counterpart [24]. Indeed, imidazoles with a methyl group at

Table 7 Electronic energies, zero-point energies and methyl cation affinities ($-\Delta H_{298}$) for substituted imidazoles. The methyl group is at position 3. Values are in kcal mol^{-1}

Molecule	B3LYP/6-31+G(d)			MP2/6-31+G(d)		
	ΔE_{elec}	ΔZPE	ΔH_{298}	ΔE_{elec}	ΔZPE	ΔH_{298}
1-Ethylimidazole	136.06	−6.40	130.89	137.43	−6.1	132.52*
1-Ethyl-5-nitroimidazole	119.61	−5.83	114.93	122.40	−5.6	117.30
1-Ethyl-2,4-dinitroimidazole	98.14	−5.72	93.55	102.81	−5.6	98.33
1-Ethyl-2,4,5-trinitroimidazole	88.43	−5.41	84.10	93.61	−5.2	89.4

* A value of 131.45 kcal mol^{-1} was determined for 1-methylimidazole [22]

position 3 on the ring have been found to have higher decomposition temperatures (>220 °C) than their protonated counterparts [24]. Thus, from the various proton and methyl cation affinity data available, we can predict that alkylated imidazoles with a methyl group at position 3 and one or more nitro groups at positions 2, 4 and 5 should be the best choice for imidazolium-based ionic liquid cations, and these should form useful highly energetic ionic liquids when combined with appropriate energetic anions.

Acknowledgments Thanks are due to the University Grants Commission, New Delhi for providing financial assistance to one of the authors (UM).

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