

A computational approach to design energetic ionic liquids

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Abstract The present work deals with the theoretical estimation of ion-pair binding energies and the energetic properties of four ion pairs formed by combining the 1-butyl-2,4-dinitro-3-methyl imidazolium ion with nitrate (**I**), perchlorate (**II**), dinitramide (**III**), or 3,5-dinitro-1,2,4-triazolate (**IV**) anions. The counterpoise-corrected ion-pair binding energies were calculated for each ion pair at the B3LYP/6-311+G(d,p) level of theory. Results show that the cation–anion interaction is strongest for ion pair **I** and weakest for **IV**, indicating that the nitrate (**I**) has a greater tendency to exist as a stable ionic salt whereas the 3,5-dinitro-1,2,4-triazolate (**IV**) may exist as an ionic liquid. Natural bond orbital (NBO) analysis and electrostatic potential (ESP) mapping revealed that charge transfer occurs in all of the ion pairs, but is greatest ($0.25e$) for ion pair **I** and smallest ($0.03e$) for **IV**, resulting in ion pair **I** being the least polarized. A nucleus-independent chemical shift (NICS) study revealed that the aromaticity of the 1-butyl-2,4-dinitro-3-methyl imidazolium ion significantly increases in ion pair **IV**, indicating that this has the greatest charge delocalization among all of the four ion pairs considered. Studies of thermodynamic and detonation properties showed that ion pair **II** is the most energetic ion pair in terms of its detonation velocity ($D = 7.5 \text{ km s}^{-1}$) and detonation pressure ($P = 23.1 \text{ GPa}$). It is also envisaged that ion pair **IV** would exist as an energetic azolium azolate type ionic liquid that could be conveniently used as a secondary explosive characterized by detonation parameters D and P of 6.9 km s^{-1} and 19.3

GPa, respectively. These values are comparable to those of conventional explosives such as TNT.

Keywords Ion-pair binding energy · Nucleus-independent chemical shift (NICS) · Volume-based thermodynamics (VBT) · Ionic liquids · Counterpoise (CP) correction

Introduction

Ionic liquids are a class of compounds that are currently attracting the attention of research scientists around the world. They are considered to be the most important new family of “green” solvents that can be used as an alternative to organic solvents [1–3]; they are called “green” in the sense that they possess negligible vapor pressure, meaning that only a minimal amount of the solvent enters the atmosphere when it is used.

Ionic liquids exist as ion pairs and are sometimes categorized as supermolecules [4]. They are generally obtained when two or more molecules combine through hydrogen bonding or charge transfer, van der Waals forces, or indeed any type of noncovalent interaction [4–6]. Some ab initio calculations [7–10] have been performed on ion pairs in the gas phase, and these have revealed that the strong electrostatic interactions between the ion pairs are the major attractive force in ion pairs, rather than weak hydrogen-bond interactions. Tsuzuki et al. [11] reported that hydrogen bonds contribute only to the stabilization energies of the cation–anion pairs in $[\text{C}_2\text{mim}][\text{PF}_6]$ and $[\text{C}_2\text{mim}][\text{BF}_4]$. Spectroscopic and density functional theory (DFT) studies performed by Talaty et al. [12] on a series of 1-alkyl-3-methylimidazolium hexafluorophosphates $[\text{C}_{2-4}\text{mim}][\text{PF}_6]$ revealed the existence of H-bond interactions between fluorine atoms of the $[\text{PF}_6]^-$ and the C_2 hydrogen of the imidazolium ring. The existence of H-bonds in 1-alkyl-3-

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methylimidazolium-based ionic liquids has also been reported by many other workers [13–15].

Most of the work performed on ionic liquids has focused on the imidazolium ring, as the latter is quite stable and can be tailored to yield the desired properties [16]. The structure of 1-butyl-3-methylimidazolium ion, [BMIM]⁺, is shown in Fig. 1. It exhibits a delocalized 3-center-4-electron configuration across the N1–C2–N3 moiety, a double bond between C4 and C5, and weak delocalization in the central region [13]. The C2 carbon is more positively charged due to the electron deficiency of the C=N bond, whereas C4 and C5 are almost neutral [14], and the hydrogen on the C2 carbon acts as a good hydrogen-bond donor [16, 17].

We selected [BMIM]⁺ as a cation to design energetic ionic liquids, and attempted to increase its energy content by introducing two nitro groups (explosophores) onto the imidazolium ring [18–20]. This substitution leads to the potential for three isomers: 2,4-, 2,5-, and 4,5-dinitro-BMIM. The 2,4-dinitro derivative of imidazole has been found to be more stable than the 2,5 and 4,5 isomers [21], and 2,4-dinitroimidazole is already known to be an energetic molecule with the potential to be applied as a relatively insensitive and thermally stable explosive [22, 23]. The two electron-withdrawing nitro groups on the C2 and C4 atoms of [BMIM]⁺ reduce the charge density on the cation, giving it more carbocation character, leading us to predict that this derivative binds strongly with anions through electrostatic interactive forces. Also, nitro group substitution leads to an increase in the bulk of the BMIM cation, which is one of the criteria for forming ionic liquids [24]. This dinitro-BMIM (1-butyl-2,4-dinitro-3-methyl imidazolium) cation may exist in four different resonance structures, as shown in Fig. 2. The charge distributions for these resonance structures suggest that they are relatively stable. Structures C and D contribute the least, as both of the nitrogens in the imidazole ring are positively charged. When the other two structures A and B are compared, the only difference is that N1 and N3 have a lone pair and a positive charge, respectively, in A, whereas the opposite is true in B.

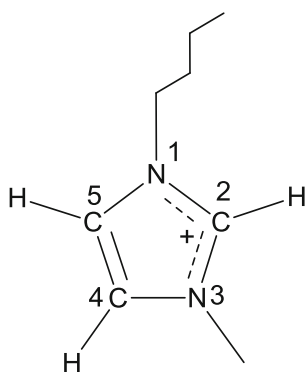


Fig. 1 1-Butyl-3-methylimidazolium ion, [BMIM]⁺

Butyl has a dominant +I (inductive) effect in comparison to the methyl group, so structure A, which has a lone pair at N1, would be destabilized due to more electron transfer from the butyl group, whereas structure B would be stabilized because of the presence of positive charge at N1. This shows that structure B is the most stable of all four resonating structures.

In the work described in the present paper, we studied the nature and characteristics of the ion pairs formed by pairing the designed cation with energetic anions such as nitrate, perchlorate, dinitramide, and 3,5-dinitro-1,2,4-triazolate. In each case, the ion-pair binding energy was determined [25–29]. Natural population analysis (NPA) [30, 31] was performed to estimate the charge distributions of and the charge transfer in the ion pairs. The electrostatic potential (ESP) was mapped onto a density isosurface to obtain a three-dimensional picture of the charge distributions of the ion pairs. The HOMO–LUMO energy gap and molecular orbital composition of each ion pair were determined in order to elucidate the molecular orbital interactions.

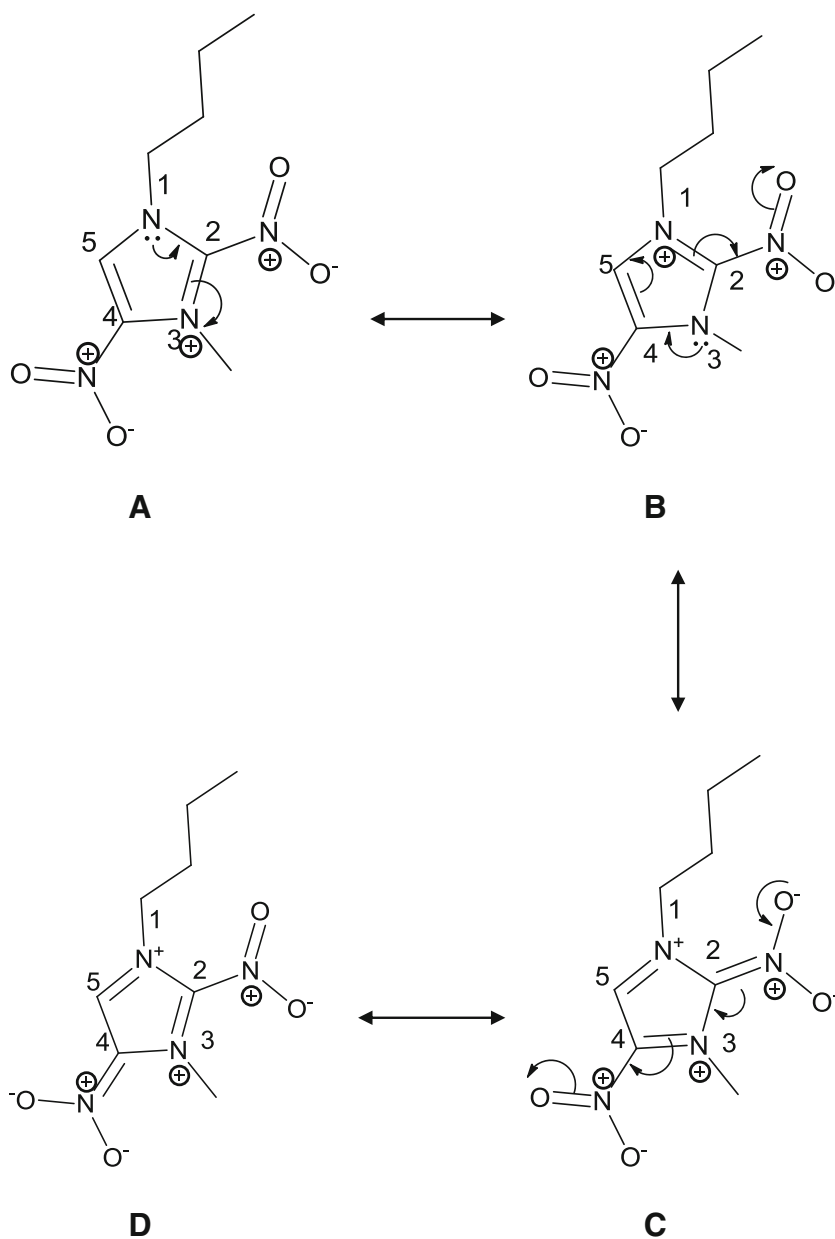
In order to assess the aromaticity of the ring system, nucleus-independent chemical shift (NICS) [32, 33] studies were performed on the ion pairs (I–IV). Significant negative values imply aromaticity (diatropic ring current), whereas positive values correspond to antiaromaticity (paratropic ring current).

In addition to the above, the thermodynamic properties and energetics of these ion pairs were evaluated at the G2 level of theory. Attempts were made to calculate these properties in the condensed phase. In order to achieve this goal, the lattice potential and lattice enthalpy were evaluated to calculate the heat of formation of each ion pair in the solid phase. Detonation properties such as the detonation pressure (*P*) and detonation velocity (*D*) were calculated and the results are compared with known commercial explosives such as TNT and RDX to assess the potential of the designed ionic salts/ionic liquids as high energy density materials.

Methods

All calculations were performed with the Gaussian 09 software package [34]. The optimized structures of the ion pairs formed as a result of pairing the 1-butyl-2,4-dinitro-3-methyl imidazolium ion with four different anions were determined at the DFT(B3LYP)/6-311+G(d,p) level of theory, and are shown in Fig. 3. The vibrational frequencies were also determined for the optimized structures to check that the structures corresponded to minima on their respective potential energy surfaces (PESs), which was achieved by verifying that all of the vibrational frequencies were real and positive.

Fig. 2 Resonance structures of the 1-butyl-2,4-dinitro-3-methylimidazolium ion



Ion-pair binding energy

The ion-pair binding energies of the ion pairs were calculated with the aid of the following expression:

$$\Delta E(AB) = E^{AB} - [E^A + E^B], \quad (1)$$

where E^A and E^B represent the energies of the cation and the anion, respectively, and E^{AB} is the energy of the ion pair. The binding energies thus determined were corrected for the basis set superposition error (BSSE) using the counterpoise (CP) correction method. The counterpoise-corrected ion-pair binding energies were calculated using the following expression [35]:

$$\Delta E^{CP}(AB) = \Delta E(AB) + \delta_{AB}^{BSSE}, \quad (2)$$

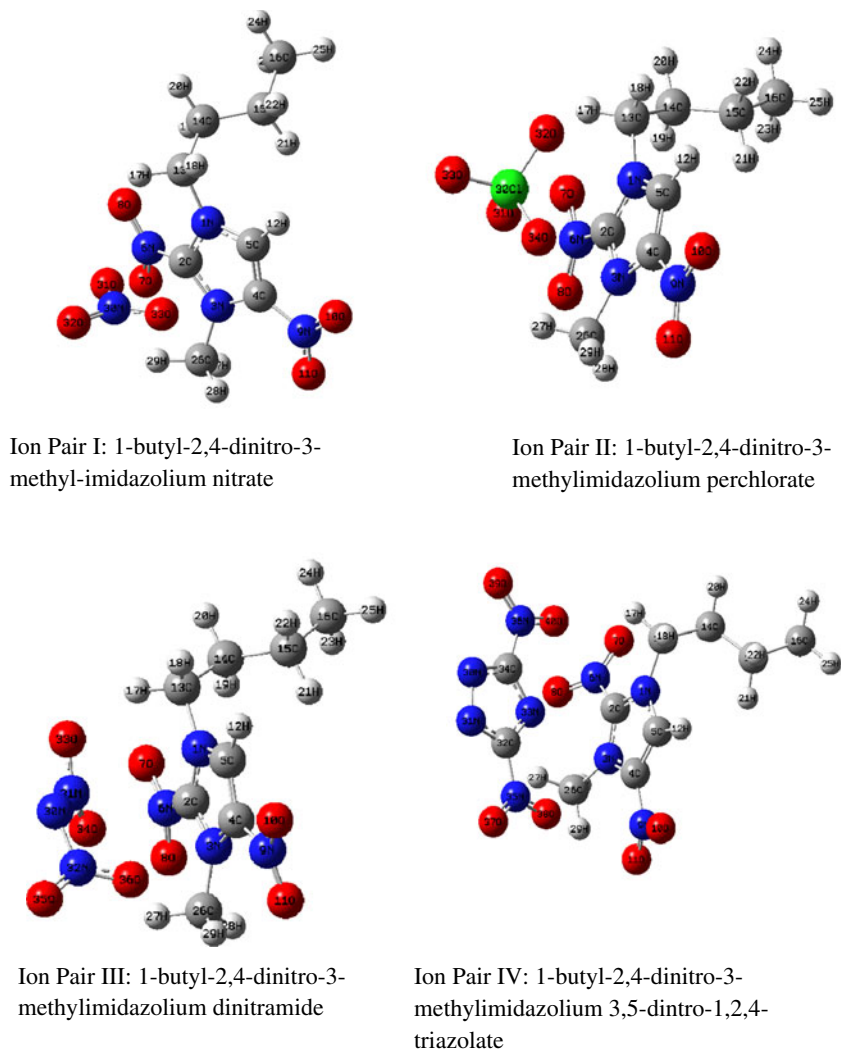
where the counterpoise correction is expressed as δ_{AB}^{BSSE} .

Electronic structure studies

Electrostatic potential (ESP) mapping onto a 0.0004 electron density isosurface (the default value in Gaussian 09) was performed for the ion pairs. Molecular orbital (MO) analysis was also carried out, and the frontier molecular orbital energies and their compositions were evaluated.

NICS calculations were performed at the center of the imidazole ring and 1 Å above/below the ring for all of the systems using the gauge-invariant atomic orbital (GIAO) [36] approach. It was found that the NICS values determined at the geometrical center of the ring—labeled NICS

Fig. 3 Optimized structures of the ion pairs obtained at the DFT/(B3LYP)/6-311+G(d,p) level



(0)—were not an accurate indicator of aromaticity, so the NICS(1) values measured 1 Å above/below the plane of the ring (which essentially reflected π effects) were selected as they were more indicative of the ring current [37, 38] and thus the aromaticity of the cation.

Heat of formation

The heat of formation is often treated as an indicator of the energy content of explosive material. In order to determine the potential utility of these ionic salts/liquids as energetic materials, the heats of formation of these species were determined in the solid phase. To do this, it was necessary to evaluate the lattice potential energy and lattice enthalpy. Volume-based thermodynamics [39] has been shown to be a reliable approach to use to estimate the lattice energy and hence the heat of formation of a salt in the condensed phase [40–44]. In this approach, calculating the ΔH_f^0 of a salt M_pX_q [45] involves determining the following parameters:

(a) U_{POT} (lattice potential energy).

The lattice potential energy of the salt was calculated using the following equation [46]:

$$U_{\text{POT}} = \gamma [(\rho/g - \text{cm}^{-3}) / (M/g)]^{1/3} + \delta, \quad (3)$$

where $\gamma = 473.5 \text{ kcal mol}^{-1} \text{ cm}$, $\delta = 24.8 \text{ kcal mol}^{-1}$, and M is the mass (in g). The density (ρ , in g cm^{-3}) in Eq. 3 was determined from the molecular volume V_m (in cm^3) of the salt M_pX_q using the equation

$$\rho/g - \text{cm}^{-3} = (M_m/g) / (V_m/\text{cm}^3), \quad (4)$$

where M_m is the molecular mass (in g). The molecular volume V_m of the salt was taken to be the sum of the volumes of the cations and anions present in the formula M_pX_q [46], which can be written

$$V_m = pV_{M^+} + qV_{X^-}. \quad (5)$$

The ionic volumes V_{M^+} and V_{X^-} were estimated using a Monte Carlo method based on a density space of 0.001 a.u. (electrons/bohr³), as implemented in Gaussian 09. The ionic volumes of the respective ions were estimated by averaging the results of 100 single-point calculations performed at the DFT (B3LYP)/6-311++G (d, p) level. Density calculations based on this approach sometimes yield significant errors. However, modifications were made, and the resulting approach was validated for molecular and ionic solids [47]. In order to estimate the ionic volumes in the present case, the same procedure was employed for the conceptually designed ionic salts/liquids as has already been successfully employed to estimate the molecular volumes of high-nitrogen compounds [48–51]. In order to gauge the reliability of the estimated molecular volumes attained via the Monte Carlo method, the volumes of the ionic salts were estimated by Hofmann’s elemental method [52, 53]:

$$V_m(\text{ionic salt}) = aV(C) + bV(H) + cV(N) + dV(O) + eV(Cl), \tag{6}$$

where the V parameters are the volumes of the individual elements that constitute the ionic salt; these values were obtained from [44] and were taken to be: C = 0.0138, H = 0.00508, N = 0.0118, O = 0.01139, Cl = 0.0258. a , b , c , d , and e are the number of atoms of the corresponding elements present in the formula of the ionic salt.

(b) ΔH_L (lattice enthalpy).

The lattice enthalpy of the salt can be written as [54]

$$\Delta H_L = U_{\text{POT}} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT, \tag{7}$$

where n_M and n_X depend on the nature of the ions M^{q+} and X^{p-} , and are equal to 3 for monoatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. p and q are unity for 1:1 salts, so the above equation can be simplified to

$$\Delta H_L = U_{\text{POT}} + 2RT. \tag{8}$$

The heat of formation of the ionic salt was then calculated using the following equation:

$$\Delta H_f^0(\text{ionic salt, 298K}) = \Delta H_f^0(\text{cation, 298K}) + \Delta H_f^0(\text{anion, 298K}) - \Delta H_L, \tag{9}$$

where the ΔH_f^0 parameters for the cation and the anions are the gas-phase heats of formation of the species calculated at the G2 level using the atomization procedure [55].

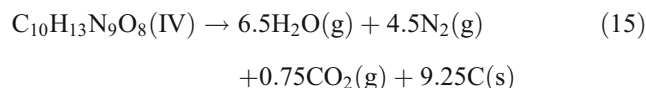
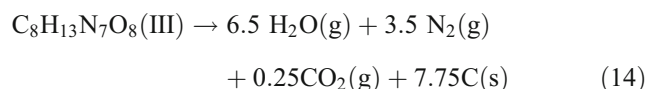
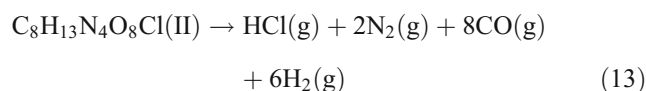
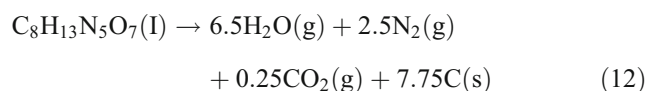
Detonation properties

The detonation velocity (D) and detonation pressure (P) are the two most important parameters for evaluating the explosive characteristics of energetic materials. The following empirical equations proposed by Kamlet–Jacobs [56] were used to calculate these two parameters:

$$D = 1.01(N M^{1/2} Q^{1/2})^{1/2} (1 + 1.30 \rho_0) \tag{10}$$

$$P = 1.56N M^{1/2} Q^{1/2} \rho_0^2, \tag{11}$$

where D is the detonation velocity (in km s⁻¹), P is the pressure (in GPa), N is the number of moles of gaseous detonation products (in mol g⁻¹), M is the average molecular weight of the gaseous products (in g mol⁻¹), Q is the heat of detonation, representing the chemical energy (in cal g⁻¹), and ρ_0 is the initial density (in g cm⁻³). N , M , and Q are determined as per the “most exothermic principle,” in which all nitrogen atoms are converted to N₂ molecules, the O atoms form H₂O with H atoms first, and any remaining O forms CO₂ with C atoms. Any C atoms remaining when all of the O atoms have been bound into molecules exist in the solid state. On the other hand, if O atoms are left over when all of the C atoms have been bound into molecules, these remaining O atoms will combine into O₂ molecules. The idealized pathways for calculating these quantities for the ion pairs **I–IV** are given by the following reactions:



In order to determine the detonation parameters using the Kamlet–Jacobs equations (Eqs. 10 and 11), Q and ρ must be known. However, for the unsynthesized and conceptual compounds considered during the present study, Q and ρ cannot be measured experimentally. In this case, Q can be determined as the difference between the heats of formation

(HOFs) of the products and reactants in the reactions of ion pairs **I–IV** (i.e., reactions 12–15), and ρ can be replaced with the theoretical density determined via Eq. 4.

Oxygen balance (OB%)

The oxygen balance (OB%) represents the percentage of the compound that must be oxygen that must be required in order to achieve complete conversion of the carbon to carbon dioxide, the hydrogen to water, and the metal to metal oxide during combustion [56]. Compounds can have negative or positive oxygen balances, leading to under- or over-oxidation, respectively. Explosive characteristics such as the sensitivity, strength, and brisance of an explosive are relatively good when OB% is zero or near to zero, although there are many exceptions to this generalization. OB% is calculated using the following equation:

$$\text{OB}\% = \frac{-1600}{M_w} (2X + Y/2 - Z), \quad (16)$$

where M_w is the molecular weight of the compound, and X , Y , and Z are the number of C, H, and O atoms present in the molecular formula of the compound, respectively.

Results and discussion

Ion-pair binding energies

Since HF excludes the electron correlation, a DFT method was employed to estimate the ion-pair binding energies. Counterpoise-corrected binding energies of the ion pairs (**I–IV**) were calculated at the B3LYP/6-311+G(d, p) level of theory, and the results are recorded in Table 1. The data show that the binding energy decreases with increasing anion size. This may be attributed to a decrease in the anion charge density with increasing ionic radius [25]. Results further show that, out of the four anions considered during the present study, the smallest anion (nitrate), which participates in ion pair **I**, possesses the highest binding energy ($-96.77 \text{ kcal mol}^{-1}$), whereas the largest anion, 3,5-dinitro-

1,2,4-triazolate, which participates in ion pair **IV**, shows the lowest binding energy ($-76.91 \text{ kcal mol}^{-1}$). The perchlorate and dinitramide anions come second and third, respectively, in terms of their anionic size/radius, and conform to the trend mentioned above, with binding energies of -87.31 and $-84.42 \text{ kcal mol}^{-1}$, respectively.

The reduction in the electrostatic strength due to charge delocalization can be correlated with the interaction energy, as it has been shown that aromatic ionic liquids (such as imidazolium-based ionic liquids) present lower interaction strengths than their saturated counterparts [25]. The lower the interaction energy for a particular ion pair, the greater the charge delocalization of that ion pair, causing a decrease in the electrostatic attraction between the cation and the anion, meaning that the ion pair would be more likely to exist as an ionic liquid. On the basis of the above discussion, we can conclude that charge delocalization is greatest in ion pair **IV**, which would therefore be the most likely to exist as an ionic liquid. In contrast, ion pair **I**, in which the charge delocalization is smallest, may exist as an ionic salt.

The ion-pair binding energy can also be correlated with the melting points of the ion pairs. In an earlier study, it was shown that the smaller the ion-pair binding energy, the lower the melting point [25]. This qualitative relationship between ion-pair binding energy and melting point can be used to theoretically predict the trend in the melting point across the series of ion pairs studied in the present work. Based on the values recorded in Table 1, it is envisaged that the melting points of ion pairs **I–IV** follow the trend **I** > **II** > **III** > **IV**.

Charge distribution

The charge distributions of the isolated cation and anions and the ion pairs (**I–IV**) were determined by NPA and the results are given in Table S1 of the “Electronic supplementary material” (ESM). The computed values show that the N1 and N3 atoms in $[\text{BMIM}]^+$ have significant negative charges (-0.34), whereas the C4 and C5 atoms are marginally negatively charged (-0.007). The only positively charged atom in the ring is the C2 atom ($+0.30$). When two strongly electron-withdrawing nitro groups are attached to $[\text{BMIM}]^+$ to form the dinitro-BMIM cation, the positive charge on the C2 atom is almost doubled ($+0.30$ to $+0.58$), while the negative charges on the N1 and N3 atoms decrease slightly. Thus, the overall effect of substituting two nitro groups is to decrease the negative charge and increase the positive charge throughout the ring, giving it increased carbocation character. Analysis of the data recorded in Table S1 of the ESM also reveals that the negative charges on N1 and N3 and the positive charge on C2 are greater in all of the ion pairs than in the dinitro-BMIM cation. These increased charges are most pronounced for ion pair **I** and least

Table 1 Ion-pair binding energies, BSSEs, and CP-corrected binding energies of ion pairs **I–IV**, calculated at the B3LYP/6-311+G(d,p) level. Energy values are in kcal mol^{-1}

Ion pair	Ion-pair binding energy	BSSE	CP-corrected ion-pair binding energy
I	-98.84	2.07	-96.77
II	-90.81	3.50	-87.31
III	-87.23	2.81	-84.42
IV	-79.77	2.86	-76.91

pronounced for ion pair **IV**. This makes C2 an attractive site for electrostatic interaction with the anion. The analysis shows that there is net decrease in the positive charge of the dinitro-BMIM cation from 1 to $0.74e$ (**I**), $0.91e$ (**II**), $0.91e$ (**III**), and $0.96e$ (**IV**). The same conclusion was drawn from the results obtained regarding the NPA charge distributions of the anions in different ion pairs, as given in Table S2 of the ESM. The calculated dipole moments of the ion pairs recorded in Table S2 show that ion pair **I**, which shows the greatest charge transfer ($0.250e$), yields the lowest dipole moment (8.28 D), while ion pair **IV**, with the least charge transfer ($0.038e$), shows the highest dipole moment (14.10 D), which is also in accord with the conclusion drawn by Hunt et al. [14]. It has been pointed out that there is a rough correlation between the amount of charge transferred and the relative stability of the ion pair. Thus, we can predict that ion pair **I**, which has the

greatest charge transfer among all four ion pairs, is more stable than the other ion pairs considered. The low charge transfer seen for ion pair **IV** is consistent with it having the lowest ion-pair binding energy among the ion pairs, which means that it probably exists as an azolium azolate type of ionic liquid.

The electrostatic potentials (ESPs) of ion pairs **I–IV** and the dinitro-BMIM ion were mapped onto a 0.0004 (the default value in Gaussian 09) electron density isosurface, as shown in Fig. 4. This ESP mapping showed that polarization of the imidazolium occurs in each ion pair, and that the polarization follows the trend **I** < **II** < **III** < **IV**. Greater polarization indicates lower charge transfer, so ion pair **I**, which shows the least polarization among all of the ion pairs, could be predicted to have the greatest charge transfer. This observation is consistent with the NPA and ion-pair binding energy studies.

Fig. 4 Electrostatic potentials calculated at the B3LYP/6-311++G(d,p) level and mapped onto the 0.0004 electron density isosurface for the cation and for ion pairs **I–IV**

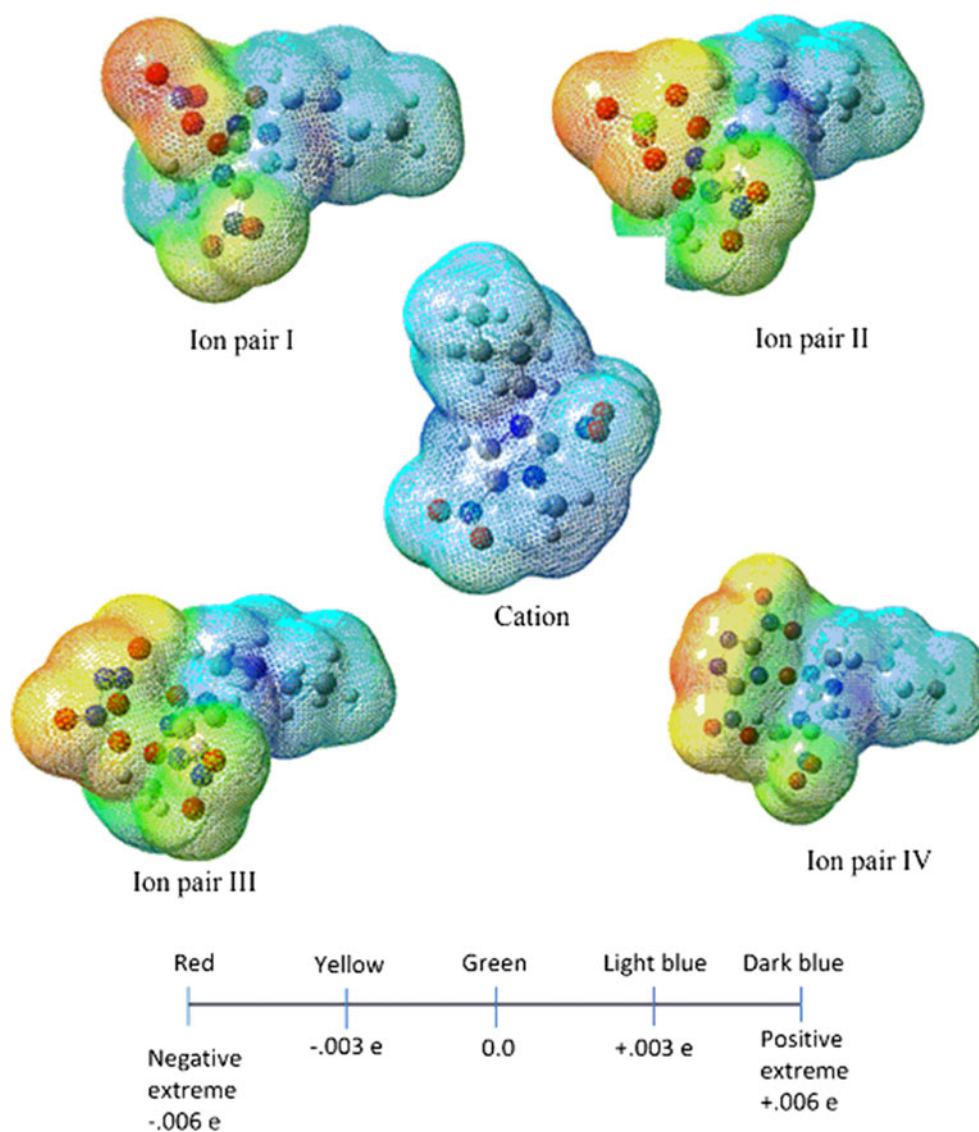


Table 2 NICS values for the cation and related species calculated at the B3LYP/6-311+G(d,p) level

Species	NICS(1)
[BMIM] ⁺	−9.81
Dinitro-BMIM ⁺	−10.11
I	−10.26
II	−9.13
III	−9.56
IV	−12.04

Nucleus-independent chemical shift (NICS)

A NICS study was performed to predict the aromatic character of the designed dinitro-BMIM cation investigated in this work. Results calculated for the NICS(1) values of [BMIM]⁺, the dinitro-BMIM cation, and ion pairs **I–IV** are recorded in Table 2. These show that the dinitro-BMIM cation has a more negative NICS(1) value than [BMIM]⁺, indicating that it has greater aromaticity. This may be attributed to the two nitro groups attached to the imidazolium ring, which maintain the aromatic sextet in the ring, as demonstrated by the resonance structures shown in Fig. 2. When this cation is paired with anions, its enhanced aromaticity is maintained, as shown by the NICS(1) values recorded in Table 2. The results show that there are slight decreases for the perchlorate (**II**) (~10%) and dinitramide (**III**) (~5%), whereas ion pair **I** has almost the same value as that of the dinitro-BMIM cation. On the other hand, for ion pair **IV**, in which the dinitro-BMIM cation is paired with the aromatic 3,5-dinitro-1,2,4-triazolate anion, enhanced aromaticity of the cation is observed. This increase may be attributed to the large size of the anion, which is a diffusely charged species. As discussed earlier, the larger the anion, the more its charge density is delocalized, which is in turn reflected in its low ion-pair binding energy and a decrease in the electrostatic attraction between the ions. Thus, we can conclude that cations with enhanced aromaticity have increased charge delocalization and lower ion-pair binding energies, ultimately leading to a reduction in the Coulomb force between the ions. Based on the above discussion, we can conclude that ion pair **IV**, which possesses the cation with the greatest aromatic character among the cations in the ion pairs, is most likely to exist as a stable ionic liquid.

Table 4 Ion pair volumes V_m (in cm³ mol^{−1}) calculated using Gaussian (B3LYP/6-311++G(d,p)) and Hofmann's elemental volumes (HEV) method

Ion pair	V_m (Gaussian)	V_m (HEV)
I	199.47	196.87
II	210.89	212.50
III	220.26	218.75
IV	251.60	250.62

Molecular orbital analysis

The frontier molecular orbitals (FMOs) and the corresponding energies of the anions, cation, and the ion pairs (**I–IV**) are recorded in Table 3. The results show that ion pair **II** has the largest HOMO–LUMO energy gap (0.105 a.u.), whereas **III** has the smallest (0.085 a.u.). A small band gap between HOMO and LUMO makes it easier for electrons to cross the gap, leading to a poor compound stability [57, 58]. Thus, the stabilities of these ion pairs, as judged based on the HOMO–LUMO energy gap, follows the order **II** > **I** > **IV** > **III**. From the calculated orbital compositions shown in Table 3, it is also clear that the LUMO of each ion pair is essentially the LUMO of the cation (accounting for ~90% of the LUMO in each case), whereas the HOMO of each ion pair is mainly a mixture of the *s* orbital of the cation and the *p* orbitals of the anions. It is worth noting that the HOMO of ion pair **IV** is almost entirely contributed by the anion (~91%). This dominant contribution from the anion is provided by its *s* orbital (~35%) as well as the its *p* orbitals. The above molecular orbital analysis therefore shows that significant orbital interactions occur in ion pairs, giving rise to moderate covalent character [17].

Thermodynamic properties

The heat of formation is an important thermodynamic property of energetic compounds that is related to their characteristic detonation properties, such as detonation velocity (*D*) and detonation pressure (*P*). A volume-based approach (described briefly in the “Methods” section) was applied to determine the

Table 3 Molecular orbital energies and their compositions in the ion pairs. Calculations were performed at the B3LYP/6-311++G(d,p) level

Ion pair	HOMO (a.u.)	LUMO (a.u.)	$\Delta E_{\text{LUMO-HOMO}}$ (a.u.)	Cation		Anion	
				HOMO %	LUMO %	HOMO %	LUMO %
I	−0.249	−0.152	0.097	64.86 (26.7 <i>s</i> 13.6 <i>p_z</i>)	90.69	35.14 (8.5 <i>p_x</i> 13.1 <i>p_y</i> 9.6 <i>p_z</i>)	9.31
II	−0.275	−0.170	0.105	65.76 (36.0 <i>s</i>)	92.48	34.24 (12 <i>p_x</i> 11.7 <i>p_y</i>)	7.52
III	−0.255	−0.170	0.085	48.23 (27.1 <i>s</i>)	91.80	51.77 (12.2 <i>s</i> , 15.7 <i>p_y</i>)	8.20
IV	−0.266	−0.174	0.092	9.22	89.71	90.78 (34.6 <i>s</i> , 23.9 <i>p_x</i> , 19.3 <i>p_y</i>)	10.29

Table 5 Thermodynamic properties of the cation, anions, and the ion pairs at 298 K

ΔH_f^0 (cation) ^a (kcal mol ⁻¹)	Anions	ΔH_f^0 (anion) ^a (kcal mol ⁻¹)	Ion pair	Density (ρ , in g cm ⁻³)	U_{POT}^b (kcal mol ⁻¹)	ΔH_L^b (kcal mol ⁻¹)	ΔH_f^0 (ion pair) ^c (kcal mol ⁻¹)
165.47	Nitrate	-76.52	I	1.46	105.77	106.96	-18.02
	Perchlorate	-58.35	II	1.56	104.36	105.54	1.58
	Dinitramide	-33.47	III	1.52	103.41	104.60	27.39
	3,5-Dinitro-1,2,4-triazolate	-10.21	IV	1.54	99.62	100.80	54.45

^a Values were calculated at the G2 level of theory for the gas phase

^b Values were calculated by the VBT method

^c Values were calculated for the condensed phase

ΔH_f^0 values. The molar volumes of ion pairs **I–IV** obtained from Gaussian as well as Hofmann's elemental volume calculations [52] are recorded in Table 4. The molar volumes calculated by both of these methods show good agreement, giving us confidence in the calculations performed by Gaussian. The densities of the ion pairs, calculated by Gaussian based on the molar volumes, are recorded in Table 5. All four ion pairs have similar densities of about 1.5 g cm⁻³, with only marginal variations. The data recorded in Table 5 also include the lattice energies for the ion pairs, which lie in the range 100–106 kcal mol⁻¹. This is quite consistent with results obtained previously for a 1:1 salt, which were reported to be in the range 96–144 kcal mol⁻¹ [54]. Table 5 also lists the calculated heats of formation of the isolated cation, anions, and the ion pairs (**I–IV**), along with the values of U_{POT} and ΔH_L . Taking into account the ΔH_L values, we evaluated the heats of formation, ΔH_f^0 (298 K), of the ionic salt in the condensed phase. The lowest value was obtained for the nitrate ion pair (-18.02 kcal mol⁻¹) and the highest for the dinitrotriazolate ion pair (54.45 kcal mol⁻¹). The only negative ΔH_f^0 (ionic salt, 298 K) value was observed for the nitrate ion pair (**I**), which we presume to be the most stable of all four ion pairs considered. From these results, we can conclude that the heat of formation increases as the number of nitrogens in the anion of the ion pair increases. Perchlorate (which does not contain nitrogen) has the lowest $\Delta_f H^0$.

The calculated detonation parameters (D and P) of the ion pairs are listed in Table 6, along with other energetic characteristics such as oxygen balance (OB%) [56] and the

heat of detonation (Q). In all cases, the oxygen balance was found to be negative, indicating that these ion pairs are oxygen deficient (underoxidized). The detonation velocities and the detonation pressures of the ion pairs are in the ranges 6–7 km s⁻¹ and 17–23 GPa, respectively. The largest values of D and P are predicted to occur for the perchlorate ion pair (**II**), which could be expected, as this ion pair also possesses a slightly higher density than the other ion pairs (see Table 5), and the detonation parameters are strongly dependent on density [59]. Table 6 also provides values for conventional explosives such as TNT and RDX [60–62] and ammonium perchlorate (monopropellant) for the sake of comparison. The present study reveals that the ion pairs considered in this work have the potential to be used as energetic materials.

Conclusions

The ion-pair binding energies and the electronic structure data obtained from NBO analysis suggest that amongst all of the ion pairs considered in the present investigation, the nitrate ion pair (**I**) is the most stable and is the most likely to exist as an ionic salt. The thermodynamic stability of this salt can also be deduced from the negative of its value of ΔH_f^0 . The results for charge transfer and orbital interactions indicate that there are some covalent interactions, even though the cation–anion interactions in these ion pairs are mainly electrostatic in nature. Although the perchlorate ion pair (**II**) provides the best

Table 6 Detonation properties of ion pairs

Ion pair or explosive	OB (%)	Q (cal g ⁻¹)	D (km s ⁻¹)	P (GPa)
I	-85.22	1309.72	6.7	17.83
II	-70.62	715.34	7.5	23.18
III	-69.25	1273.24	7.0	19.76
IV	-76.48	1293.59	6.9	19.32
TNT	-74.00	1090.8 [57]	6.93 [58]	21.00 [59]
RDX	-43.00	1510.99 [57]	8.75 [58]	34.10 [59]
NH ₄ ClO ₄ (AP)	+34.00 [44]	–	6.44 [44]	15.60 [44]

energetic performance and has good thermal stability, its environmental impact (one of the major decomposition products of the perchlorate ion pair is carbon monoxide; see Eq. 13) makes it less attractive as a high-energy material. The dinitramide (III) and the dinitrotriazolate (IV) ion pairs have comparable energetic performances and densities. Based on studies of the NBO, ion pair-binding energies, and NICS, we can conclude that ion pair IV is the most likely of these ion pairs to exist as an azolium azolate type of ionic liquid. This is supported by its high positive heat of formation and its more environmentally friendly nature than ion pair II, indicating that it could be a promising high-energy ionic liquid.

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