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Neutral species from "non-protic" N-heterocyclic ionic liquids†

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Possible isomerisation of 1,2,3-trialkylimidazolium and 1-alkylpyridinium ion pairs by proton transfer and by the nucleophilic addition of the anion to the cation have been investigated at the B3LYP/6-31+G* and B3LYP/6-311+G** levels of density functional theory. The deprotonation energies of 1,2,3-trialkylimidazolium and 1-alkylpyridinium cations to diaza-pentafulvene and pyridinium-ylide, respectively, were only slightly larger than that of 1,3-dialkylimidazolium salts yielding N-heterocyclic carbenes. Accordingly, in the case of 1,2,3-dialkylimidazolium salt ion pairs the stability of the H-bonded complex between the fulvene and the corresponding acid can be comparable to that of the ion pair in the presence of sufficiently basic anions, such as acetate. In the case of the pyridinium salts the nucleophilicity of the cation dominates over the acidity, and the formation of 1,2- or 1,4-dihydropyridine derivatives is preferred over proton transfer.

Introduction

Ionic liquids[1] (ILs) have an exceptionally wide variety of applications due to their high stability, non-flammability, low volatility and their unique solution properties. These substances are often classified as protic and non-protic ILs,[1k] according to the availability of acidic protons in their cation. Although compounds of both classes can be purified by distillation,[1k,2] their evaporation mechanism is considered to be basically different. In protic ILs the acidic proton is easily transferred to the anion, thus the vapour of these species consists of neutral acids and bases.[1k,3] From non-protic ILs, however, single ion pairs were observed as evaporated species in different experiments.[2,4]

Our recent photoelectron spectroscopic measurements, together with DFT calculations revealed that the "non-protic" 1,3-dialkylimidazolium-based **1a′** ion pair isomerises to a neutral H-bridged N-heterocyclic carbene (NHC)-acid pair **1b′** (Fig. 1) in the presence of sufficiently basic anions, such as acetate.[5] Furthermore, under higher vacuum conditions—like in the ionization chamber of a mass spectrometer—this H-bonded structure can dissociate to the free carbene **2′** and the corresponding acid.[5a] This evaporation process is similar to that of protic ILs,[1k,3] showing that the "strict" distinction between protic and non-protic ILs should be considered with care. In the liquid phase the ionic isomer (**1a′**) is stabilized, due to the mutual coulomb interactions between the surrounding charged particles.[5a] Nevertheless, the presence of NHCs in ILs is clearly indicated by the formation of palladium complexes when palladium acetate is dissolved in imidazolium-based ILs.[1n,6a–b] Very recently, the corresponding carbenes could be trapped from these ILs by chalcogens, forming imidazole-2-chalcogenones.[6c] Accordingly, the "protic nature" of an ionic liquid depends not only on the cation, but the cation/anion assembly. This unexpected observation prompts an apparent question: are there any other cation–anion pairs which can form neutral species by proton transfer?

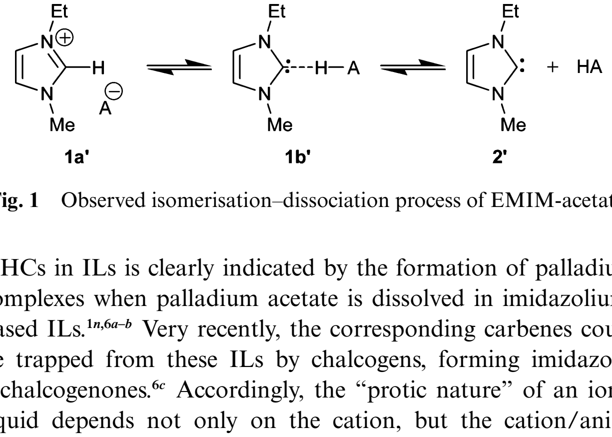

Fig. 1 Observed isomerisation–dissociation process of EMIM-acetate.

Interestingly, there are some scattered literature data suggesting that neutral species are obtainable from other "non-protic" ILs. 1,3-Dialkyl-2-methylimidazolium cations (**3′**) were shown to undergo deprotonation by alkali hydrides.[7a] This process—which is similar to the most common synthetic route[1n,8] employed to form imidazol-2-ylidenes[9] (**2′**)—yields diaza-pentafulvene derivatives **4′** (Fig. 2).[7a] This deprotonation at the 2-methyl group has also been observed indirectly in D_2O *via* H/D exchange, in the presence of amine bases.[1n,7b] Moreover, deprotonation of 3-decyl-1,2-dimethylimidazolium salts has been reported to occur also at surfaces containing the basic silicate anion, albeit at rather high temperatures (400–550 °C).[10] All these data suggest the possibility to generate derivatives of **4′** from 1,3-dialkyl-2-methylimidazolium-based ILs, in the presence of sufficiently basic anions.

Interestingly, in the presence of bases (pyridine, acetate anion) and metal ions, pyridinium cation **5′** has been reported to form

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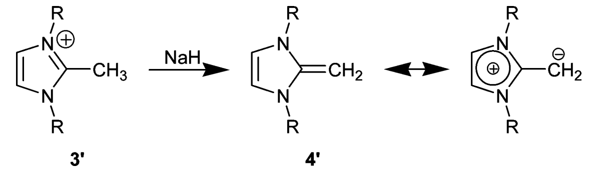


Fig. 2 Deprotonation of 1,3-dialkyl-2-methylimidazolium cation.

complexes of pyridine-2-ylidene **6′**.[11] Likewise in the analogous reaction of the imidazolium salt **1a′** (see above),[6] this reaction should involve the free carbene **6′** (Fig. 3), and the presence of **6′** as an intermediate has also been reported in different reactions.[12] Thus, the proton transfer in pyridinium-based ILs is also a viable possibility. Recently we have shown, that by the deprotonation of **5′** the formation of pyridinium-ylide **7′** (Fig. 3) is preferred instead of **6′**.[13] Although the relative stabilities are somewhat varied by substitution at the ring carbons and the nitrogen, derivatives of **7′** were generally found to be more stable than **5′** by a few kcal mol^{-1}.[13]

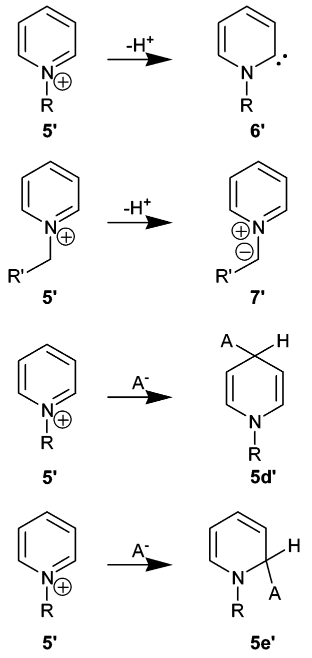


Fig. 3 Possible generation of neutral species from pyridinium salts.

In the case of pyridinium salts, not only deprotonation takes place in the presence of bases. With OH^-, CN^-, NH_2^- anions, nucleophilic attack of the counteranion on the carbon atoms at positions 2 or 4 of the pyridine ring has been reported (**5d′** and **5e′**, Fig. 3),[14] and also the reaction with BuLi results in butylation,[14] thus, for the sake of completeness these isomers should also be considered.

Although the amount of these neutral compounds in the liquid is presumably small, their accessibility may modify the microscopic structure, thus the physical (viscosity, melting point, vapor pressure, spectra) and chemical (solubility, catalysis, stability) properties of ILs. Accordingly, such behavior of ILs is worth to be considered and explored prior to application. In this study, the formation of the neutral species **4′**, **5d′**, **5e′**, **6′**, **7′** from 1,3-dialkyl-2-methylimidazolium and pyridinium-based IL ion pairs has been investigated computationally to gain a general picture of the extent of these isomerisation processes in the presence of different anions.

Models and methods

In our previous study[5a] we have shown that the length of the side chain attached to the nitrogen atoms of 1,3-dialkylimidazolium ion pairs has only a slight effect on the relative energy of the different isomers, and the results obtained for 1,3-dimethylimidazolium salts can be used for modeling *e.g.* 1-ethyl-3-methyl derivatives. H-bonded complexes between the acid and all possible deprotonated products have been investigated for fluoride, acetate and hydroxide anions, but those having high relative energies have been omitted for other anions (see Supporting Information†).

All calculations have been carried out with the Gaussian 03 program package.[15] For the 1,3-dimethylimidazolium ion pairs B3LYP/6-31+G* level data have been shown[5a] to be in reasonable agreement with the experiments and with results obtained at other levels of theory, *underestimating* somewhat the stability of the H-bonded **1b** with respect to the ion pair **1a**, thus, we applied this method for full geometry optimizations also in this study. At the optimized structures the eigenvalues of the Hessian have been calculated to confirm the nature of the stationary point obtained, providing positive numbers only. Measures of aromaticity have been calculated at the B3LYP/6-311+G** level.

Results and discussion

To compare the accessibility of the aforementioned deprotonated neutral species, deprotonation energies of the model cations have been calculated, together with those of the previously investigated **1** (Fig. 4).

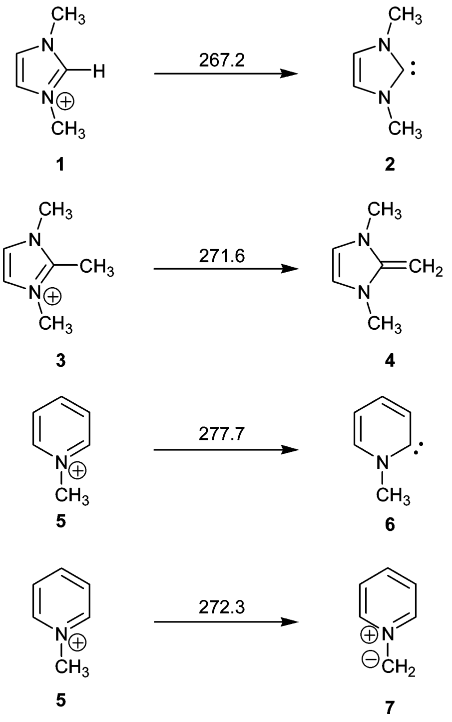


Fig. 4 B3LYP/6-31+G* deprotonation energies of **1**, **3** and **5** (in kcal mol^{-1}).

The accessibility of the so-called "remote" carbenes[16] and the occurrence of H/D exchange at position 4 of imidazolium derivatives[17] suggest that deprotonation of **1** and **3** at the backbone of the ring might also be feasible. However, the deprotonation energy at that position of **3** (289.7 kcal mol^{-1}) is by 18.1 kcal mol^{-1} larger than that at the 2-methyl group. The deprotonation energy at the N-methyl group—yielding a structure analogous to pyridinium-ylides—is even larger (297.7 kcal mol^{-1}), thus, in the further calculations only the formation of **4** is considered.

Unexpectedly, the deprotonation energy of **3** at the methyl group is similar to that of **1** at position 2. This indicates considerable stability for the fulvene **4**. Indeed, **4′** (R = H) has been reported to exhibit some aromaticity as concluded from the GIAO-HF/6-31-G*//B3LYP/6-31G* NICS(0) value[18] (–6.8),[19] which can be rationalized by an ylidic structure (Fig. 2). Accordingly, the rotational barrier of the methylene moiety has been shown to be lower than for "genuine" double bonds (30.6 kcal mol^{-1} for **4′** R = H and 50.2 kcal mol^{-1} for 1,1-diaminoethene at the MP2/6-31G* level).[20] It is worth to note that for the rotational barrier of the phosphorous ylide $H_3P{=}CH_2$ only 1.2 kcal mol^{-1} has been reported,[21] showing that the rotational barrier is not necessarily related to the strength of the ylidic bonding.

To further evaluate the contribution of aromaticity to the deprotonation energy of **3**, the Isomerisation Stabilization Energy (ISE) approach[13,22] has been applied for **4**, and also NICS(1),[18] exaltation of the magnetic susceptibility[23] ($\Delta\Lambda$, in the ISE reaction), Bird-index (BI)[24] and Bond Shortening Index (BDSHRT)[25] have been calculated (Table 1).

The ISE reaction for **4** can be seen in Fig. 5, which indicates a stabilization energy of –4.0 kcal mol^{-1} (B3LYP/6-311+G** level). This value is by *ca.* 10 kcal mol^{-1} lower than that for **2**.[13] In agreement, BDSHRT and NICS values also show reduced aromaticity for **4** with respect to **2**.

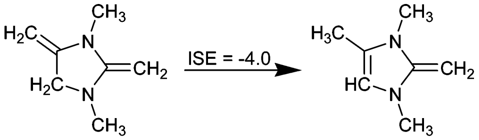


Fig. 5 ISE reaction for evaluating the aromaticity of **4** (B3LYP/6-311+G**, in kcal mol^{-1}).

The relative energies of the species obtainable by the deprotonation of type **5** structures have previously been investigated computationally,[13] and **6** and **7** analogues have been shown to be the most stable isomers. The formation of **7** from **5** is by 5.4(7.1)[13] kcal mol^{-1} more favourable than that of **6** at the B3LYP/6-31+G* and B3LYP/6-311+G** (in parenthesis) levels. While the stability of **6** has been partly attributed to its aromaticity,[13] little is known about the electronic structure of **7**, although some pyridinium ylides with π-electron withdrawing substituents at the methylene group,[26] were studied before computationally. The ylidic character with an inversely polarized C–N bond is clearly seen by the partial atomic charges shown in Fig. 6.

Table 1 Aromaticity measures of **4** and **2**

	ISE	NICS(0)	NICS(1)	$\Delta\Lambda$	BI	BDSHRT
2	−13.1	−11.3	−9.3	−6	61	48
4	−4.0	−8.9	−4.3	−3	52	43

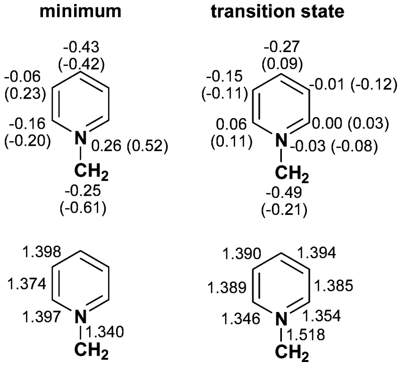


Fig. 6 B3LYP/6-311+G** Mulliken and APT (in parenthesis) charges, and bond lengths (lower row) of pyridinium-ylidene **7** and its rotational transition state.

Interestingly, however, not only the CH_2 unit exhibits negative charge, but the ring carbon atoms are also negatively charged, indicating that the electronic system is fully delocalized, as noted also before.[26] A clear indication for the delocalization is the planarity of the CH_2 unit, however, little back donation was shown by the topological analysis of the electron density.[26b] In the delocalization, the nitrogen lone pair is fully involved, participating with a significant contribution in two low lying unoccupied orbitals (see Figure S1 in the Supporting Information†) but not in the HOMO (Fig. 7). Accordingly, the $(H_2)C$–N bond has little double bond character, as was noted by investigating the bond distance before.[26] A similar conclusion can be drawn from the electron density at the $(H_2)C$–N bond critical point in **7** (ρ = 0.307), which is between that of methylamine and methanimine (ρ = 0.261 and 0.388, respectively). Interestingly, the isoelectronic aniline has similar electron density at the C–N bond critical point (ρ = 0.296). These data are in agreement with the conjugated nature of the π-system. Interestingly, the polarization of the conjugated π-system in **7** highly affects the aromaticity of the ring, which is significantly reduced compared to **5** according to the NICS,[18] BI[24] and BDSHRT[25] aromaticity measures (Table 2).

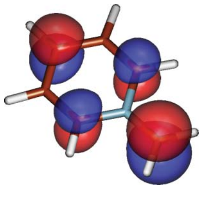


Fig. 7 HOMO of **7**.

In the transition state of the rotation around the C–N bond, however, the π-system is less polarized (Fig. 6), and this structure

Table 2 Aromaticity measures of **5**, **7** and the rotational transition state of **7**

	NICS(0)	NICS(1)	BI	BDSHRT
5	−7.9	−10.0	86	61
7	−0.2	−2.0	64	55
7(TS)	−7.3	−9.9	86	61

Table 3 Dissociation energies[28] of the **3a**, **3b**, **3c** structures containing different anions to **4** and the corresponding conjugate acid at the B3LYP/6-31+G* level (in kcal mol^{-1})

		E_{diss}		
		Ion pair	H-bonded	Adduct
Anion	E_{prot}	**3a**	**3b**	**3c**
$\mathbf{CF_3SO_3^-}$	–301.7	50.0	—	—
$\mathbf{Cl^-}$	–328.1	30.8	—	—
$\mathbf{ClCH_2COO^-}$	–334.9	24.8	—	—
$\mathbf{CH_3COO^-}$	–349.2	16.8	9.5	—
$\mathbf{SH^-}$	–351.1	9.3	3.6	—
$\mathbf{CN^-}$	–353.2	5.1	5.5	5.9
$\mathbf{F^-}$	–366.0	10.3	13.6	17.6
$\mathbf{CH_3O^-}$	–384.8	—	6.2	3.5
$\mathbf{OH^-}$	–392.5	—	6.5	9.6
$\mathbf{H^-}$	–447.5	—	0.2	20.8

exhibits aromatic properties similar to that of **5** (see Table 2). The B3LYP/6-311+G** rotational barrier (28.1 kcal mol^{-1}) is much higher than that for the isoelectronic aniline (5.5 kcal mol^{-1}), and is close to that of **4** (28.3 kcal mol^{-1}). Also the different ISE values (for their detailed discussion, see the Supporting Information†) are between 20 and 30 kcal mol^{-1} showing that the delocalized but non-aromatic electronic structure of **7** is significantly stabilized. Such asymmetric electron delocalization with significant stabilization is known also for cyclic phosphorus ylides,[27a] where an external pseudo-π center interacts with the π-system of the ring. Likewise in the case of **7**, also for σ^4,λ^5-phosphabenzene ($C_5H_5PH_2$), near zero NICS(0) (–1.3) and NICS(1) (–2.5) values were reported.[27b]

The aforementioned stabilizing effects in **4**, **6** and **7** apparently contribute to the deprotonation energies, which are, therefore, similar for all **1**, **3** and **5** (267–273 kcal mol^{-1}). Thus, 1,3-dialkyl-2-methylimidazolium- and pyridinium-based ILs are likely to exhibit similar (albeit somewhat reduced) proton transfer behaviour to 1-ethyl-3-methylimidazolium acetate.

1,2,3-Trimethylimidazolium salts

In Table 3, dissociation energies[28] of some 1,2,3-trimethylimidazolium salt ion pair isomers (Fig. 8) to **4** and the conjugate acid of the anion are presented for different anions. Likewise in the case of **1a–c**,[5a] the relative stabilities of the isomers and their dissociation energies can be related to the basicity of the anion, and three groups can be distinguished.

In the case of anions with low basicities (E_{prot} > *ca.* –340 kcal mol^{-1}) only the corresponding ion pair **3a** could be optimized, and all attempts to optimize **3b** and **3c** resulted in this structure. While in the most stable isomers of **1a** the anion is oriented either to the H(2) or the C(2),[5a,29] (these two structures have similar energy), in the case of **3a** the preferred position of the anion is above the ring, in an apparent interaction with the C(2) and the N-methyl groups (**3a$_1$**, see Fig. 9). For most of the anions two further isomers could also be obtained with the anion oriented either to the methyl hydrogens and H(4) (**3a$_2$**) or to H(4) and H(5) (**3a$_3$**), having higher energies (Fig. 9). Dissociation energies[28] to the neutral **4** and the acid are in the same range as for the corresponding **1a** derivatives[5a] (*e.g.* for **1a** (A = $CF_3SO_3^-$) 46.7 kcal mol^{-1}), indicating similarly strong interactions between the oppositely charged ions.

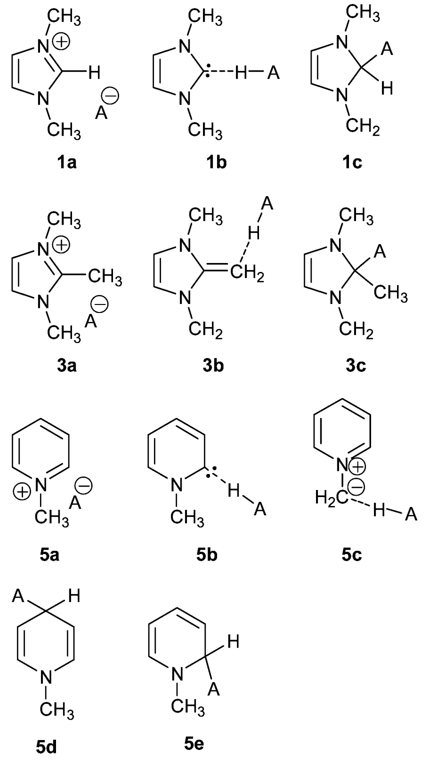


Fig. 8 The examined isomers of the model structures.

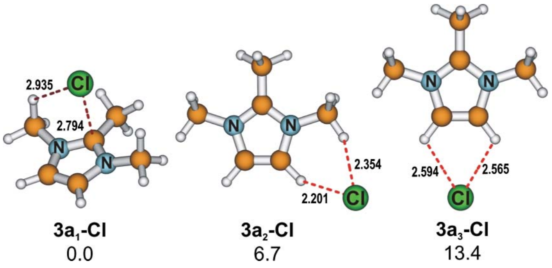


Fig. 9 Optimized structure of 1,2,3-trimethylimidazolium-chloride isomers, and their B3LYP/6-31+G* level relative energies (kcal mol^{-1}).

For moderately basic anions (–340 > E_{prot} > –370 kcal mol^{-1}) both the ionic **3a** and the fulvene-type **3b** structures could be optimized. In **3b** the acid is oriented with its acidic hydrogen toward the methylene moiety, forming apparently an H-bond (Fig. 10) with **4**, which has been justified by localizing the corresponding bond critical point. The presence of these species can be rationalized by the above discussed polarized, ylidic bonding situation of the exocyclic double bond in **4** (Fig. 2), with negative charge at the methylene moiety, which was also shown before by NBO and charge decomposition analyses.[19]

The barrier of the **3a$_1$-Ac** → **3b-Ac** isomerisation is 9.6 kcal mol^{-1}, which is somewhat higher, than that for the **1a** → **1b** analogue (3.6 kcal mol^{-1}),[5a] presumably due to the larger difference in relative stabilities. Nonetheless, this barrier suggests that the proton transfer is a viable process also at room temperature.

Although the dissociation energies[28] are smaller than those of **1b** (for **1b** (A = acetate) 15.4 kcal mol^{-1} was calculated),[5a] the 9.5 kcal mol^{-1} obtained for **3b** (A = acetate) is still larger than the strength of the hydrogen bond between two water molecules (6.4 kcal mol^{-1} at the same level). Nevertheless, these bond energies

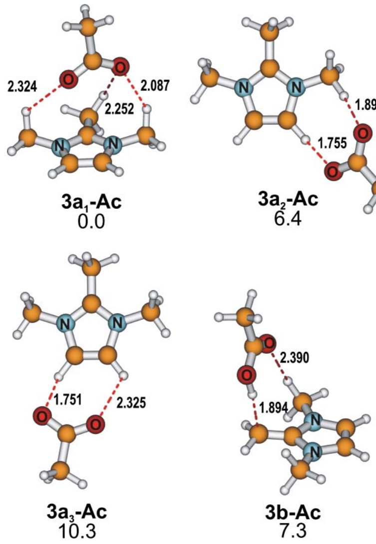


Fig. 10 Optimized structure of 1,2,3-trimethylimidazolium-acetate isomers, and their B3LYP/6-31+G* level relative energies (kcal mol^{-1}).

can be exceeded[5a] by the effect of dissociation entropy, thus, the formation of the fulvene **4** is conceivable at higher temperatures and under low pressure, in agreement with the results of MS experiments at silicate surfaces.[10]

3c structures could only be optimized in the case of F^- and the strongly nucleophilic CN^- ion in this group, resulting in the most stable isomers, similarly to the previous observations regarding **1c** compounds.[5a]

In the group of the most basic anions ($E_{prot} < -370$ kcal mol^{-1}), both **3b** and **3c** structures could be obtained (Fig. 11), and the optimizations starting from ion pair type structures resulted in one of these isomers. Thus, a single 1,2,3-trimethylimidazolium-hydroxide ion pair is unlikely to exist in the gas phase or in non-polar media. Similar results were reported for 1,3-dimethylimidazolium-hydroxide.[5a,31c,32] The electron density at the C–H(A) bond critical point in the case of **3b** (A = OH^-)—the complex of **4** with water—is $\rho = 0.024$. This value is comparable to the $\rho = 0.035$ in **1b** A = OH^-, and $\rho = 0.028$ between two water molecules, indicating a surprisingly strong H-bond with a methylene moiety.

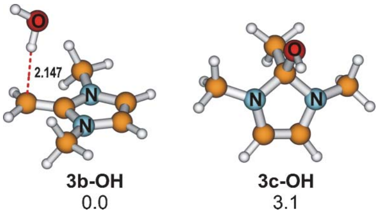


Fig. 11 Optimized structure of 1,2,3-trimethylimidazolium-hydroxide isomers, and their B3LYP/6-31+G* level relative energies (kcal mol^{-1}).[30]

As an extreme case the 1,2,3-trimethylimidazolium hydride has also been calculated. Since its "conjugate acid" dihydrogen is unpolar, no hydrogen bond is formed with **4**, and the dissociation energy for the corresponding type **3b** structure (**4** + H_2) is negligibly small (note that the data in Table 3 are BSSE[28] uncorrected).

Clearly, with the increasing basicity (and nucleophilicity) of the anion, the **3b** type structures are stabilized with respect to **3a**. The dissociation energy of **3b** is small, in accordance with the hydrogen bond between fulvene **4** and the acid, and for most of the type **3b** structures the dissociation energies are within the same range. The, dissociation energies of adduct **3c** clearly depend on the nucleophilicity of the anion, which generally increases with basicity, thus, for more basic anions those structures are the most stable isomers.

Table 4 Dissociation energies[28] of the **5a**, **5b**, **5c**, **5d** and **5e** structures containing different anions to **7** and the corresponding conjugate acid at the B3LYP/6-31+G* level (in kcal mol^{-1}). The dissociation to **6** and the conjugate acid takes more energy by 5.4 kcal mol^{-1}

		E_{diss}				
		Ion pair	H-bonded		Adduct	
Anion	E_{prot}	**5a**	**5b**	**5c**	**5d**	**5e**
$CF_3SO_3^-$	−301.7	49.1	—	—	—	—
Cl^-	−328.1	35.8	—	—	—	—
$ClCH_2COO^-$	−334.9	26.9	—	—	24.3	26.2
CH_3COO^-	−349.2	20.0	—	8.8	22.4	24.9
SH^-	−351.1	—	1.1	2.9	24.8	25.5
CN^-	−353.2	5.9	4.2	4.2	29.6	26.7
F^-	−366.0	19.5	—	12.6	28.7	32.0
CH_3O^-	−384.8	—	5.8	4.5	22.8	25.9
OH^-	−392.5	—	6.0	4.7	22.7	26.0
H^-	−447.5	—	−4.9	0.3	36.3	35.4

1-Methylpyridinium salts

Dissociation energies of pyridinium salt isomers **5a–e** (Fig. 8) to the neutral ylide **7** and the corresponding acid can be seen in Table 4 for different anions.

In the case of the weakly basic anions ($E_{prot} > -340$ kcal mol^{-1}), only the ion pair **5a** could be optimized, except for the chloroacetate, in which case also the adducts **5d–e** could be found, indicating the stability of the covalently bound **5d** and **5e** type structures. There are several accessible binding sites of the cation,[29d,33] but generally only three types of **5a** structures could be optimized (for the chloride see Fig. 12). In these isomers the anion apparently interacts with the C(2), C(4), H(2) or H(Me) atoms of the cation. According to the relative energies of **$5a_1$-Cl**, **$5a_2$-Cl**, and **$5a_3$-Cl** (Fig. 12), these interactions are similar in energy, in good accordance with previous findings regarding 1-ethyl-[29d] and 1-butylpyridinium tetrafluoroborates.[33] These structures exhibit similar dissociation energies (Table 4) compared to those for the corresponding **1b** and **3b** analogue. Considering the similar deprotonation energies of **3** and **5** (resulting in **7**) the strength of the cation–anion interactions are likely to fall in the same range as for the corresponding **1a** and **3a** structures.

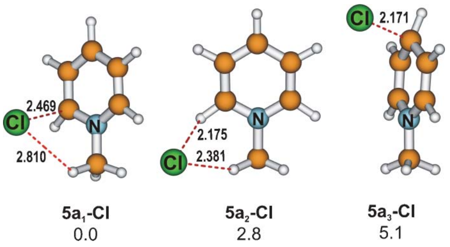
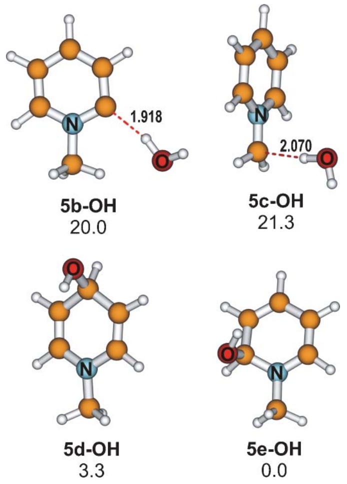


Fig. 12 Optimized structure of 1-methylpyridinium-chloride isomers, and their B3LYP/6-31+G* level relative energies (in kcal mol^{-1}).

In the case of the "moderately basic anions" (−340 > E_{prot} > −370 kcal mol^{-1}) the covalently bound type **5d** and **5e** species are remarkably stable compared to the other investigated isomers, in agreement with the experimental findings.[13] While the dissociation energy (thus the relative stability) of ion pair **5a** decreases by the increased basicity of the anion, similarly to **1a** and **3a**, those of the **5d–e** structures remains in the same range, except for the fluoride, which exhibits significantly higher affinity to the pyridinium ring. In the case of the most basic (and nucleophilic) anions these adducts become the most stable structures. It is worth to mention that the big differences (>10 kcal mol^{-1}) in stabilities between **5a** and **5d–e** structures indicate that the nucleophilicity of the cation may compete also with the solvation energy, and the adducts might form in considerable concentrations also in the liquid phase in the presence of sufficiently basic anions.

For the "moderately basic anions" H-bridged structures (**5b–c**) could also be optimized apart from the covalent **5d–e** isomers, however, **5a** structures exhibit higher stabilities than both H-bonded **5b–c** (the case of the SH$^-$ anion was exceptional, this ion pair could not be obtained). Interestingly, although carbene **6** is less stable than ylide **7** (by 5.4 kcal mol^{-1}), the energy of the **5b** and **5c** structures is nearly identical. This finding can be rationalized by the above discussed strong stabilizing interaction between the methylene group and the pyridinium ring in **7**, which is decreased by the formation of the H-bond in **5c**, resulting in some destabilization of these structures. The formation of strong H-bonds of carbenes[5a,31] with their in plane lone pairs, however does not affect the π-system. The different strength of the H-bonds in **5b** and **5c** are also clearly indicated by the bond lengths (see Fig. 13) and the electron densities at the corresponding C–H(A) bond critical points. While these values show that H-bonds with **6** are significantly stronger (*e.g.* A = OH; $\rho = 0.041$) than that with either **2** or **4**, in the case of the analogous derivatives of **7** these values are lower by *ca.* 50% (*e.g.* A = OH; $\rho = 0.022$).



5b-OH
20.0

5c-OH
21.3

5d-OH
3.3

5e-OH
0.0

Fig. 13 Optimized structure of 1-methylpyridinium-hydroxide isomers, and their B3LYP/6-31+G* level relative energies (in kcal mol^{-1}).[30]

Summary and conclusions

The formation of a variety of neutral species from 1,2,3-trimethylimidazolium and 1-methylpyridinium ion pairs is energetically possible for certain anions. For the less basic anions, the ion pairs (which are the building blocks of the ionic liquids) are the most stable species according to the DFT calculations. With the increasing basicity (and nucleophilic character) of the anion, the ion pair structure becomes destabilized and two competing processes should be considered. The energetically most favourable one in the case of trimethylimidazolium salts is the proton transfer from the cation to the anion providing diazapentafulvenes together with the acid derived from the anion. In the case of pyridinium salts, which are prone to react with nucleophiles, the addition of the anion to the cationic ring is the preferred process resulting in dihydropyridine derivatives.

Accordingly, the description of imidazolium or pyridinium based ionic liquids with basic anions as pure ionic substances is oversimplified. While in the condensed phase these ILs are built up from ions being stabilized by their mutual interaction, the presence of traces of the above mentioned neutral species should be considered, affecting by variation of the pressure and temperature the physical properties (*e.g.* evaporation or surface properties) of the liquid. Furthermore, although ILs are generally regarded as inert media for syntheses, if basic ions are present as substrates or products of the process performed in an IL, unexpected reactions may occur.

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