Triazolium-Based Energetic Ionic Liquids

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The energetic ionic liquids formed by the 1,2,4-triazolium cation family and dinitramide anion are investigated by ab initio quantum chemistry calculations, to address the following questions: How does substitution at the triazolium ring's nitrogen atoms affect its heat of formation, and its charge delocalization? What kind of ion dimer structures might exist? And, do deprotonation reactions occur, as a possible first step in the decomposition of these materials?

Introduction

Recent years have seen a great enthusiasm for ionic liquids (ILs) in regard to their utility as novel and "green" solvents,[1–3] because their ability to serve as new solvent environments is quite remarkable. IL properties include high electrical conductivities, high dielectric constants, nonexistent vapor pressures, and often excellent thermal and chemical stabilities[3] and therefore offer the prospect of hosting new catalytic behavior.[4,5] A short list of the novel solvent properties of ILs would include different systems that are either completely miscible or immiscible with water,[4] the ability to form emulsions,[6] and tuning of the dielectric constant by absorption of large mole fractions of supercritical CO_2.[7] Two recent computer simulations of 1-butyl-3-methylimidazolium (bmim$^+$)/PF$_6^-$ show at least two different time scales for diffusion in such solvents,[8] and yield information on preferred structures.[9] An experimental[10] study of the interaction of water with the surface layer of this IL, known to be immiscible with water, observed structural changes consistent with the latter simulation.

Despite this easily understandable focus on the novel solvent properties of stable ILs, it is good to remember[11,12] that ILs are neither new materials nor are they required to be stable or are limited to use as solvents. Indeed, the well-known and undesired "red oil" appearing during Friedel–Crafts reactions is an ionic liquid containing an Al$_2$Cl$_7^-$ anion. A 12 °C melting point for CH$_3$CH$_2$NH$_3^+$NO$_3^-$ was reported as early as 1914,[13] and a dark red-brown oil Et$_3$NH$^+$CuCl$_2^-$ was discovered in 1963.[14] King[15] and Wilkes[16] and co-workers investigated systems such as LiCl/AlCl$_3$ (mp 145 °C) starting in the 1960s, with the goal of developing molten liquid, high current batteries. Electrochemical properties of the 1,4-dimethyl-1,2,4-triazolium chloride/AlCl$_3$ system have been reported.[17] A key breakthrough came with Wilkes' design using MNDO theory of the 1-ethyl-3-methylimidazolium (emim$^+$) cation in 1982,[18] achieving a 25 °C melting point for emim$^+$/AlCl$_4^-$. A decade later the Wilkes group[19] investigated changing the anion to NO$_3^-$, BF$_4^-$, and acetate, with the latter freezing to a glass at −45 °C. This work helped established the current IL design principle that the very large lattice energy of a conventional salt such as NaCl (mp 801 °C) can be lowered to near or even below room temperature by using cations and anions differing in size, by delocalizing the charge within each ion to reduce point charge forces, and by exploiting asymmetrically shaped ions to entropically disrupt the lattice.[3] Many ILs used as solvents are derived from emim$^+$ in that they contain a substituted imidazolium ring, for example the increasingly popular bmim$^+$. The recent development of the bis(triflyl)amide anion[20] has made it easy to create numerous IL systems that avoid crystallization altogether, to form glasses at temperatures well below 0 °C. Very recently[21] it has been shown that amino acids can serve as the counterion to emim$^+$, demonstrating that the anion need not be inorganic. Two additional nonsolvent applications of ILs can be mentioned. One is the development of an ionic liquid crystal system.[22] Electrospray of the stable IL emim$^+$/BF$_4^-$ has been proposed for use as a highly controllable microthruster.[23–25]

Room temperature ionic liquids are normally considered chemically and thermally stable, because they are often based on the imidazolium or other stable cations, and may also contain nearly inert perfluoro anions. However, it is of interest to consider chemically unstable ionic liquids,[26] which may have interesting applications. In particular, this work will consider the use of both more energetic cations and anions. The cations considered are the triazoliums, five membered rings containing three nitrogens rather than the two found in imidazolium. Note that a dinitrosubstituted triazole was recently used as a triazolate anion in an energetic low melting salt[27] but herein we consider only triazolium cations. The anion considered replaces the stable ions used in solvents such as BF$_4^-$ or PF$_6^-$ with the energetic dinitramide ion,[28] N(NO$_2$)$_2^-$.

Accordingly, the first topic addressed in the current paper is an attempt to assess charge delocalization in triazolium ions. Second, the heats of formation of various substituted triazolium cations are predicted. Next, by considering ionic pairs (one cation and one anion), possible structure motifs in the bulk ionic liquids are probed. Finally, as a first attempt to consider the possible decomposition reactions of an energetic IL, we report on the deprotonation reactions. Relevant literature citations for each topic will be given below, as each is considered in turn. Related research on tetrazolium based energetic ionic liquids will be presented elsewhere.[29]

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TABLE 1: MP2/6-31++G(d,p) Electronic Energy Differences, in kJ/mol

	H	F	OH	NH$_2$	CH$_3$	CN	N$_3$	NF$_2$	NO$_2$	C$_2$H$_3$	OCH$_3$
1,4 isomer (R′=H) R=	0	0	0	0	0	0	0	0	0	0	0
4,1 isomer (R = H) R′=	0	16	20	21	12	0.2	22	7	16	12	22
1,2 isomer (R″ = H) R=	56	73	65	67	55	56	63	58	57	53	64

Method of Calculation

As all species considered here are closed shell in nature, the majority of the calculations are done at the closed shell Hartree−Fock (RHF)[30] or second-order perturbation theory (MP2)[31] levels. To facilitate π bonding analysis, some multi-configuration (MCSCF) calculations were carried out to access the inherent interpretability of this wave function in terms of localized active orbitals,[32] although the RHF determinant in all cases remains at least 92% of the MCSCF function. Mulliken charges[33] and charges fitted to electrostatic potentials[34] were not found to yield useful ring charge delocalization information. The basis set[35] employed for all calculations is 6-31++G(d,p), using diffuse functions on all atoms (including the cationic species) so that these functions are present for the anions. Some G2 thermochemistry calculations[36] are performed using the standard methods and basis sets employed in the construction of that model. All computations were performed with the GAMESS electronic structure package,[37,38] except the G2 calculations, which employed the Gaussian94 code.[39]

Charge Delocalization in Triazolium Cations

Triazolium based ionic liquids are typically prepared by quaternization of a triazole (often, by protonation of a triazole ring nitrogen by a strong acid), followed by a metathesis reaction to replace the anion of the generated triazolium salt by anions more suitable to forming ionic liquids. The triazole or triazolium nitrogen atoms can be located at 1,2,3[40] or 1,2,4 (see below for the IUPAC ring numbering), but only the latter is considered in the present paper. The synthesis of 4-amino-1,2,4-triazole (4AT) has been known since 1944.[41] Reactions which transform the NH$_2$ functionality at N$_4$ into various substitutions at N$_1$ are well-known; see for example ref 42. The IR spectra of the parent 1,3-imidazole H$_4$C$_3$N$_2$, 1,2,4-triazole H$_3$C$_2$N$_3$, and even tetrazole H$_2$CN$_4$ were published in 1956,[43a] developing an IR fingerprint for protonation at ring nitrogens (in 1,3 imidazolium cation). Raman spectra of chlorhydrate salts of triazolium bromide[43b] give similar fingerprints for triazolium NH ring vibrations. Recent experimental work[44] on the quaternization of 4AT shows that protonation occurs at N$_1$, and conversely, quaternization of 1-amino-1,2,4-triazole leads to protonation at N$_4$. An energetic salt (mp 95 °C) of 4AT with nitroform ion (C(NO$_2$)$_3$$^-$) was reported in 1966,[45] and triazolium salts with the energetic perchlorate ClO$_4$$^-$ were given in 1969.[46] The group of Pevzner[47] has worked on the synthesis of energetic triazoles and related compounds for two decades. More recently, Shreeve and co-workers[48−53] have reported the synthesis of numerous ionic liquids containing imidazolium, triazolium, and tetrazolium cations. A number of crystal structures of the bromide and nitrate salts of substituted triazoliums are now available.[54]

Substitution in triazolium is possible at both nitrogen and carbon atoms, with the known substituents at the N atoms being primarily H, alkyl, or NH$_2$ (in any combination at N$_1$ and N$_4$), although the interesting nitroimide (−N$^-$−NO$_2$) group has been placed at N$_4$.[55] Routes to disubstitution at N$_1$ and N$_2$ rather than the more typical N$_1$ and N$_4$ are also known.[56] Energetic substituents at carbon include both nitro (NO$_2$)[47,57] and azido (N$_3$) groups. The azido group was introduced into an azole in

1905[47] and such azoles were recently quaternized into ionic liquids.[52] It is also possible to introduce halogen at one or both carbons in the neutral triazoles; see for example ref 58. The following "back of the envelope" estimation predicts that substitution at nitrogen should give a higher heat of formation than carbon substitition. A textbook tabulation[59] of typical bond strengths shows that breaking a CH bond should cost about 25 kJ/mol more than breaking an NH bond. However, the payback for forming a C−R bond compared to an N−R bond more than recovers this cost. C−R bond energies exceed N−R bond energies by 202, 157, 58, or 41 kJ/mol, respectively, for R = C, O, N, F single bonds. Thus carbon substituted triazoliums would be expected to have lower heats of formation, and therefore only nitrogen substitution is considered here. Quantitative tests of this assumption in the tetrazolium system will be reported elsewhere.[29]

Obviously, triazolium based energetic ionic liquids are experimentally realistic,[26,47,52,53,54,60] so it is relevant to ask how substitution on the triazolium may affect their properties. The two questions about the triazolium cation that are addressed first are the charge delocalization in nitrogen substituted 1,2,4-triazolium cations, and in the next section, their gas phase thermodynamic stabilities. Recall that greater charge delocalization is considered to be a key factor in producing lower melting points. The triazolium species considered here include the more interesting 1,4-substituted compounds, but also include the 1,2-substituted forms for completeness,
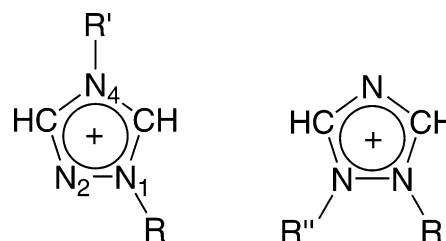
Typically only one substituent R, R′, or R″ is considered here, with the other ligand usually being H. The substituents R are chosen to include the simple series H, F, OH, NH$_2$, and CH$_3$, and more energetic groups such as CN, N$_3$, NF$_2$, NO$_2$, CH = CH$_2$, or OCH$_3$. Table 1 gives the relative energies for monosubstitution. Note that substitution at the 1 position of 1,4 isomers is always energetically favored over substitution at the 4 position, although sometimes by only a narrow margin. NMR experiments[44] show that for R = NH$_2$, the only observed cation is the 1,4 isomer, R′=H. Because the 1,2 isomers are always higher in energy, they will not be considered further (except for the inclusion of a few R = R″ = H results).

The geometry of the triazolium ring is remarkably constant. Compared to the parent 1,4-substituted triazolium, the other 1,4 and 4,1 substituted systems change the five ring bond lengths by: N$_1$−N$_2$ = −0.029 to +0.014, N$_2$−C$_3$ = −0.005 to +0.009, C$_3$−N$_4$ = −0.008 to +0.016, N$_4$−C$_5$ = −0.008 to +0.016, and C$_5$−N$_1$ = −0.004 to +0.011 Å, at the MP2/6-31++G(d,p) level.

It is now convenient to introduce the resonance forms that will be used to discuss the charge distribution in 1,4-substituted triazolium ions, and in the next section, for constructing

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TABLE 2: MCSCF/6-31++G(d,p) π Orbital Analysis

	π orbital populations						
	N_1	N_2	C_3	N_4	C_5	total bonding	MP2 energy
1,4 ion I/II	1.43	1.15	0.98	1.49	0.95	1.91	−241.932210
1,2 ion III	1.50	1.50	0.94	1.12	0.94	1.94	−241.910862
neutral IV	1.14	1.14	1.05	1.62	1.05	1.98	−241.574345
neutral V	1.59	1.20	1.03	1.16	1.02	1.95	−241.585265

	adjacent (1,2) π bonding					next neighbor (1,3) π antibonding				
	N_1−N_2	N_2−C_3	C_3−N_4	N_4−C_5	C_5−N_1	N_1−C_3	N_2−N_4	C_3−C_5	N_4−N_1	C_5−N_2
1,4 ion I/II	0.42	0.78	0.48	0.58	0.67	−0.14	−0.19	−0.18	−0.28	−0.23
1,2 ion III	0.39	0.62	0.63	0.63	0.62	−0.30	−0.20	+0.05	−0.20	−0.30
neutral IV	0.44	0.77	0.46	0.46	0.77	−0.10	−0.24	−0.24	−0.24	−0.10
neutral V	0.42	0.73	0.54	0.70	0.53	−0.21	−0.15	−0.05	−0.25	−0.31

isodesmic reactions.[61] To assess the relative importance of these resonance structures, a charge and bonding analysis of the parents (R = R′ = H) will be presented:
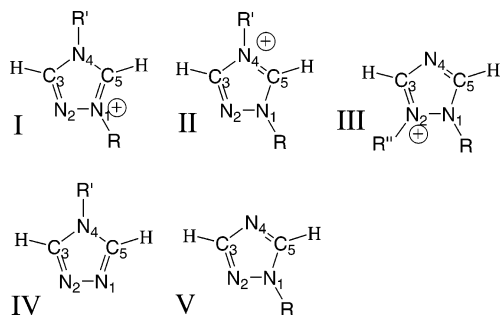
Resonance structures I and II differ in the position of double bonds, and in the location of the cationic charge. The important design criterion for ionic liquids, that they should exhibit substantial charge delocalization, therefore depends on the relative contributions these two resonance forms make to the molecular wave function. The 1,2-substituted triazolium has two equivalent resonance structures III whereas the neutral triazoles IV and V produced by deprotonation have only the single uncharged Lewis diagrams shown. All four species are 6π e$^-$ systems.

Two routine procedures for assigning atomic charges were tested. Although point charges on atoms, especially in ionic species, are suspect, "chemical intuition" might suggest that any resonance between I and II implies substantial positive charge on both N_1 and N_4. However, Mulliken population analysis[33] of either RHF or MP2 densities showed large changes at the ring atom as a function of substituent; for example the charge at N_1 for R = CN is −0.33 and for R = N$_3$ it is +0.27. Because no chemically meaningful patterns can be seen, the data are omitted. Second, fitting the MP2 electrostatic potential with atomic point charges[34] also did not give intuitive results. For example, for 10 of the 11 cases for R substitution, the charges at N_1 are 0.30−0.55, whereas N_4 actually takes on a negative value ranging from −0.21 to −0.50. For R′ substitution, the charges reverse, with N_1 quite close to zero in 10 of 11 compounds, and N_4 ranging from 0.12 to 0.27. Because both of these nitrogens are intuitively expected to be positive, these results are less than satisfying.

However, the relative importance of the resonance forms can be assessed by analysis of the MCSCF wave functions, in which the six π electrons are considered to occupy five active π orbitals. The closed shell determinant comprises 92−93% of all such MCSCF wave functions considered, but the MCSCF wave functions afford a much more revealing analysis of what the π electrons are doing than Hartree−Fock. The analysis

procedure[32] begins by localizing the five active MCSCF orbitals, resulting in five atom centered p orbitals, then regenerates the MCSCF density matrix for these atomic-like MCSCF MOs. Diagonal elements of the localized orbital density matrix may be considered to be the number of electrons occupying each particular p orbital. Off-diagonal elements are π bond orders, with positive and negative values reflecting bonding or antibonding, and with the magnitude of the number giving the strength of the interaction. Table 2 contains the results of such an analysis for the 1,4 and 1,2 dihydrogen triazolium ions, and their deprotonated forms. The energetics of deprotonation is addressed later, as the present focus is an assessment of the resonance stabilization.

If resonance structure I dominated over II, N_1 would possess one π electron, and N_4 two π electrons. Conversely, structure II assigns two π electrons to N_1 and one to N_4. Table 2 shows that N_1 and N_4 possess 1.43 and 1.49 π electrons, respectively, implying nearly equal weights for resonance forms I and II. This suggests that the formal plus charge in I and II is roughly equally shared by these two nitrogens. Similarly, N_1 and N_2 have 1.50 π electrons in the 1−2 isomer, where symmetry implies the resonance forms III must have exactly equal contribution.

The bonding analysis in the second part of Table 2 supports the implication of nearly equal resonance weights obtained from the π populations. None of the adjacent π bonding interactions is as small as 0 or as large as 1, as implied in the drawings I−V, when any particular π bond is absent or present. Focusing on N$_4$C$_5$ and C$_5$N$_1$, which exchange a π bond between resonance forms I and II, we see that neutral molecule IV has a smaller π bond order (0.46) between N$_4$C$_5$, whereas neutral V has a more complete bond here (0.70), with 1,4-triazolium being intermediate at 0.58. Similarly, the 0.67 bond order for C$_5$N$_1$ in 1,4 triazolium is also intermediate between the 0.77 and 0.53 for the neutrals.

Every next nearest neighbor interaction is slightly antibonding (negative interaction), with but one exception. This is a common characteristic in aromatic systems. For example, all para interactions in various benzene analogues are found to be antibonding,[62] and this merely reflects the inherent delocalization. If we simply sum all five bonding interactions plus all five antibonding interactions, the resulting "total bonding" interaction reported in Table 2 is remarkably close to the 2 π bonds drawn in each diagram I−V.

Table 3 reports the π populations and total bonding of various 1,4 substituted triazolium cations. It may be seen that apart from the ligands CN and NF$_2$, there are virtually constant populations at N_1 and N_4 although the values are somewhat changed from those of the parent (R = R′ = H), N_1 = 1.43 and N_4 = 1.49, reported in Table 2.
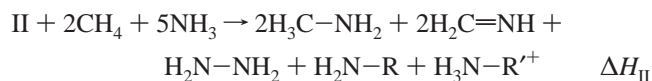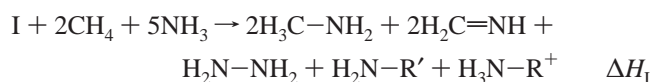
TABLE 3: MCSCF/6-31++G(d,p) π Orbital Analysis of Substituted Triazolium Cations

| | | π orbital populations | | | | | |
R	R′	N_1	N_2	C_3	N_4	C_5	total bonding
F	H	1.37	1.16	0.99	1.49	1.00	1.91
OH	H	1.32	1.17	0.99	1.52	1.00	1.92
NH_2	H	1.36	1.15	1.00	1.51	0.97	1.93
CH_3	H	1.33	1.15	1.00	1.53	1.00	1.92
CN	H	1.54	1.13	1.00	1.40	0.94	1.90
N_3	H	1.32	1.17	0.99	1.52	1.00	1.90
NF_2	H	1.48	1.13	1.00	1.44	0.95	1.92
NO_2	H	1.33	1.15	1.01	1.52	1.00	1.91
C_2H_3	H	1.33	1.15	1.00	1.52	0.99	1.92
OCH_3	H	1.31	1.16	1.00	1.53	1.00	1.93
H	F	1.44	1.14	1.01	1.43	0.99	1.91
H	OH	1.44	1.14	1.01	1.42	0.98	1.92
H	NH_2	1.44	1.14	1.02	1.43	0.97	1.93
H	CH_3	1.46	1.14	1.02	1.39	0.99	1.93
H	CN	1.34	1.13	0.98	1.60	0.95	1.92
H	N_3	1.43	1.14	1.01	1.45	0.97	1.92
H	NF_2	1.37	1.13	0.99	1.56	0.95	1.93
H	NO_2	1.46	1.15	1.01	1.40	0.99	1.90
H	C_2H_3	1.45	1.14	1.01	1.41	0.99	1.92
H	OCH_3	1.46	1.14	1.02	1.39	0.99	1.92
CN	NH_2	1.57	1.13	1.01	1.35	0.94	1.91
NH_2	CN	1.30	1.14	0.98	1.62	0.95	1.91

Taking CN rather than NF_2 from the two substituents that affect π populations, and taking NH_2 as typical of the others, two doubly substituted systems are included as the final entries in Table 3. Indeed, these two molecules seem to represent the limit to which π electron localization can be pushed onto N_1 or onto N_4. Of course low melting points are associated with charge delocalization, so the only prediction that can be made regarding lower melting points is to use ligands other than NF_2 and CN. The slightly more stable R substituted molecules appear to be a bit less charge delocalized than the R′ substituted systems. The total π bond orders of all molecules remain almost unchanged, at nearly two full π bonds in the rings.

Thermochemistry of Triazolium Cations

Speaking of energetic cations implies, of course, that their heats of formation are high. The gas phase heats of formation will be presented for both N_1 and N_4 monosubstituted triazolium ions, as this quantity is independent of the nature of the counteranion. The most efficient computational procedure for finding accurate heats of formation is based on isodesmic[61] (bond type conserving) reactions. In the present case, because there are two resonance structures I and II given above, two isodesmic reactions are considered:

$$I + 2CH_4 + 5NH_3 \rightarrow 2H_3C-NH_2 + 2H_2C=NH +$$
$$H_2N-NH_2 + H_2N-R' + H_3N-R^+ \qquad \Delta H_I$$

$$II + 2CH_4 + 5NH_3 \rightarrow 2H_3C-NH_2 + 2H_2C=NH +$$
$$H_2N-NH_2 + H_2N-R + H_3N-R'^+ \qquad \Delta H_{II}$$

These reactions differ by exchanging R and R′ in the amine and protonated amine products. By having the same number of CN single and double bonds, and NN, CH, and NH single bonds on each side of these isodesmic reactions, one hopes for improved accuracy (due to error cancellations) in the computed enthalpy of reaction, obtained in the present case by MP2/6-31++G(d,p). Combining the total reaction energy with the experimental heats of formation of all smaller molecules in these

two reactions allows extraction of a theoretical heat of formation for both I and II. It will be shown that these two heats are always very similar, and their average can therefore be taken as a heat of formation of the actual resonance hybrid of I/II.

Because many of the R groups considered here are rather unstable, many of the amine and protonated amine heats of formation are not available from experiment. These are therefore computed by the G2 procedure and compared to available experimental information, in Table 4.

The G2 energies including thermal corrections to 298 K are obtained in the standard way.[36] Experimental proton affinities[63] agree with G2 values to within the 10 kJ/mol accuracy expected for the G2 method, except for the case R = C_2H_3. Note that three of the R groups contain more favorable protonation sites than the amine nitrogen. Heats of formation for all amines and protonated amines are obtained from the G2 energies using G2 atomic energies,[36a] and G2 heats of formation at 0 K of atoms,[36b] and the standard G2 thermal corrections for atoms.[36b] A value of 1528.085 kJ/mol was used for the heat of formation of the gas-phase proton,[64] with a thermal correction of 6.197 kJ/mol (5RT/2). Experimental heats of formation[65] shown in Table 4 also agree well with the results from G2 theory, again with the exception of the vinyl substituent C_2H_3.

The computed heats of reaction for the two isodesmic reactions above are found by combining the MP2/6-31++G(d,p) energy difference for the reaction, the scaled zero point energies and other thermal factors (ideal gas, rigid rotor, harmonic oscillator partition functions), to yield a theoretical $\Delta H°(298)$ for reactions 1 and 2. Given the G2 derived heats of formation presented in Table 4, it is easy to extract the heats of formation of the resonance forms I and II, and then their average value, which are presented in Table 5.

The only comparison with experiment that is possible is for the parent, R = R′ = H, for which the experimental heat of formation is 835 kJ/mol.[65] The closeness of the present computed result, 822 kJ/mol, to this value is encouraging. Note that very similar heats of formation are derived from the isodesmic reaction of each resonance structure, with NO_2 having the largest variation at 36 kJ/mol. This suggests that the averaged heats of formation given in Table 5 may be taken as an estimate of the heat of formation, in the gas phase, of the monosubstituted triazolium cations. As already noted with regard to the 0 K energy differences given in Table 1, substitution at N_4 is slightly higher in energy than at N_1. Although all of the energies in Table 5 are large positive numbers, because they are gas-phase reference states, on a per weight basis the parent and the two very energetic groups N_3, CN stand out. Note, however, that the experimentally accessible protonated 4AT (R = NH_2) is close behind this trio. Perhaps the most realistic synthetic target for high energy content suggested by Table 5 is CN substitution at nitrogen, because N_3 substitution would require creating a ring *exo* NN single bond. The rest of this paper concentrates on two cations, namely the parent and NH_2 substitution at N_4, because of their high energy content and their experimental existence.

Ion Deprotonation and Protonation Energetics

Pairs of ions, either the parent 1-H,4-H-1,2,4-triazolium or 1-H,4-NH_2-1,2,4-triazolium cation combined with a dinitramide anion, and the proton-transfer reactions between these are considered in the next section. Here, the energy costs for deprotonating either ring hydrogen from an isolated triazolium, and the energy gains for protonating an isolated dinitramide

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TABLE 4: G2 Energies, Proton Affinities, and Heats of Formation of Amines and Protonated Amines, at 298 K[a]

						RNH$_2$		RNH$_3^+$	
			PA	PA′	PA′	ΔH_f	ΔH_f	ΔH_f	ΔH_f
R	G2(RNH$_2$)	G2(RNH$_3^+$)	G2	exp	G2	G2	exp	G2	exp
H	−56.454841	−56.777598	847.4	853.6		−47.6	−45.9	626.4	630
F	−155.529266	−155.817447	756.6			−33.2		732.1	
OH	−131.529103	−131.837695	810.2			−47.3	−42	664.4	
NH$_2$	−111.676216	−112.003327	858.8	853.2		96.7	95.4	759.7	770
CH$_3$	−95.662525	−96.003321	894.8	899.0		−25.4	−23.0	601.7	611
CN	−148.554808	−148.817548	689.8	805.6	810.8	135.7	134	967.8	
N$_3$	−219.783477	−220.087659	798.6			418.8		1142.1	
NF$_2$	−309.883456	−310.162220	731.9			−27.8		762.2	
NO$_2$	−260.702675	−260.976511	719.0	757.4	746.6	−5.8		797.1	
C$_2$H$_3$	−133.686373	−134.012498	856.2	898.9	917.7	55.9	29	721.5	
OCH$_3$	−170.740391	−171.060178	839.6	844.8		−34.6	−26	647.7	

[a] G2 total energies are in hartree, and all other energies are in kJ/mol. PA is the proton affinity at the amine nitrogen, whereas PA′ is the proton affinity at the preferred protonation site (when different). The G2 energies for CH$_4$ and H$_2$C=NH are −40.407060 and −94.459413, respectively.

TABLE 5: Heats of Formation in kJ/mol at 298 K for Gas Phase Monosubstituted 1,2,4-Triazolium Cations, at 298 K[a]

	for R′ = H cations					for R′ = H cations			
			average					average	
R	$\Delta H_f°$(I)	$\Delta H_f°$(II)			R″	$\Delta H_f°$(I)	$\Delta H_f°$(II)		
H	822.2	822.2	822	11.7	H	822.2	822.2	822	11.7
F	895.2	904.8	900	10.2	F	920.4	910.8	916	10.4
OH	809.4	822.1	816	9.5	OH	842.9	830.2	837	9.7
NH$_2$	898.0	905.4	902	10.6	NH$_2$	927.0	919.6	923	10.9
CH$_3$	770.6	773.7	772	9.2	CH$_3$	786.2	783.1	785	9.3
CN	1108.3	1109.1	1109	11.7	CN	1109.6	1108.8	1109	11.7
N$_3$	1272.8	1288.8	1281	11.5	N$_3$	1310.9	1294.9	1303	11.7
NF$_2$	919.5	940.4	930	7.7	NF$_2$	947.4	926.5	937	7.7
NO$_2$	971.9	935.6	954	8.3	NO$_2$	951.7	987.9	970	8.4
C$_2$H$_3$	878.9	884.4	882	9.2	C$_2$H$_3$	898.1	892.6	895	9.3
OCH$_3$	798.4	809.9	804	8.0	OCH$_3$	831.7	820.2	826	8.2

[a] I and II refer to particular resonance hybrids, with their average values being the predicted heats. The average is given in both kJ/mol and kJ/g.

TABLE 6: Cation Deprotonation and Anion Protonation Energetics (kJ/mol)[a]

deprotonate at N$_1$: 1,4-triazolium → 4-triazole + H$^+$	927
deprotonate at N$_4$: 1,4-triazolium → 1-triazole + H$^+$	901 (exp = 886[63])
deprotonate at N$_2$: 1,2-triazolium → 1-triazole + H$^+$	846
protonate at central N: N(NO$_2$)$_2^-$ + H$^+$ → HN(NO$_2$)$_2$	−1312
protonate at terminal O: N(NO$_2$)$_2^-$ + H$^+$ → N(NO(OH))NO$_2$	−1293

[a] Values are $\Delta H°$(298 K), in kJ/mol.

anion at all possible sites are presented, as these factors combine to determine the energetics of most of the ion and neutral pair geometries located.

The energies required to deprotonate 1-H,4-H or 1-H,2-H substituted triazolium cations, to produce all possible neutral products can be found in Table 6. These energies were obtained by combining the MP2 total energies of the ions and neutrals given in Table 2 with MP2 zero point energies and thermal corrections. The tabulated experimental value[63] of the proton affinity of 1-H-1,2,4-triazole is in reasonably good agreement with the computed value, but experiment does not give the preferred protonation site. The primary literature[66] cited by the standard table[63] used MP2/6-31G(d,p) energies at RHF/STO-3G geometries to interpret their experimental result, finding an energy preference of 58 kJ/mol for protonation at N$_4$ over N$_2$, nearly identical to the 55 kJ/mol reported in Table 6. A much older paper[43b] using CNDO/2 electrostatic potentials leads to the same conclusion, that 1-H-1,2,4-triazole preferentially protonates at N$_4$ rather than N$_2$. However a recent paper[67] using B3LYP/6-311+G(3df,3pd) at B3LYP/6-31G(d,p) structures reported a theoretical gas-phase basicity attributed to protonation at N$_2$, which is quite possibly a typographical error.[68]

Deprotonation from N$_1$ in 1-H,4-NH$_2$-1,2,4-triazolium cation requires 941 kJ/mol, compared to the 927 kJ/mol required for the parent, so N$_4$ amine substitution might affect the hydrogen bonding ability of the more tightly bound N$_1$ hydrogen.

Table 6 also contains data for the protonation of the energetic ion dinitramide,[28] N(NO$_2$)$_2^-$. This ion is considered here because in addition to its high energy content, it has several sites for the negative charge to delocalize, and therefore triazolium and 4-amino-triazolium cations form a low melting salt and an oil, respectively, when combined with dinitramide anion.[26] It is known from theoretical calculations[28] that the free dinitramide ion has a C_2 geometry, but Raman spectra[28] show that it is found in dinitramide salts without any local symmetry. Protonation of dinitramide has previously been considered,[69] and the present results are essentially the same. Protonation at the central nitrogen, giving a structure without any symmetry, is favored by 19 kJ/mol over protonation at the terminal oxygens. There are four isomers for protonation on the terminal oxygens, all of which have C_s symmetry, with the NO$_2$H group coplanar with the plane of the three nitrogens. The most stable of these has the H atom on the oxygen atom trans to the other NO$_2$ group,

which is perpendicular to the N_3 plane,
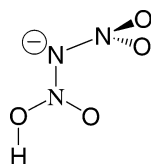
so the energy of this isomer was used in Table 6. Trial structures with the proton placed near the N of an NO_2 group optimized toward protonation at the oxygens. Both the dinitramide ion and its protonated forms are found to be rather flexible, being able to rotate NO_2 groups and deform various bend angles.

Note that the protonation energy of dinitramide is larger than the deprotonation energy of triazolium cations, indicating that the anion may be able to pull a proton away from the cation, a theme that will be developed in the next section.

Structures of Triazolium and Dinitramide Ion Pairs

Now consider the possible dimer geometries for a single triazolium cation and a single dinitramide anion. This is closely related to simulations of both small clusters and bulk materials by the Thompson group for the explosive materials ammonium nitrate,[70-72] ammonium dinitramide,[73-76] and hydroxylammonium nitrate.[77] This research,[75] and earlier computations on ammonium dinitramide in the Morokuma group,[78] show that one NH_4^+ cation and one dinitramide anion spontaneously transfer a proton to produce neutral products. Although a minimum for an ionic dimer pair exists at the RHF level,[78] both MP2[78] and DFT[75] computations find that only a hydrogen bonded, neutral pair $(NH_3)(HN(NO_2)_2)$ exists. However, this is due to the small size of the ion dimer cluster, as the ion tetramer $(NH_4^+)_2(N(NO_2)_2^-)_2$ or even the ammonia adduct to the ion dimer $(NH_4^+)(N(NO_2)_2^-)NH_3$ are minima on the correlated potential energy surfaces, due to increased numbers of strong Coulombic interactions.[75]

Although there is no question that bulk materials will consist of ionic species, these dimer proton transfer reactions and the neutral pairs that result are likely to be a primary decomposition mechanism, because decomposition probably occurs simultaneously with vaporization. Alavi and Thompson[79] have studied the decomposition of protonated dinitramide, $HN(NO_2)_2$, and related systems such as its parent anion and ammonium complexes, and give references to earlier, relevant experimental and theoretical work. They find that the two experimentally observed channels for ammonium dinitramide decomposition, N_2O or NO_2 products, each have an activation energy of about 145 kJ/mol, but that N_2O product can be formed from the solid-state ionic structures, whereas the NO_2 channel opens only after vaporization leads to proton transfer to neutral precursors.

In addition to their relevance to the decomposition of energetic ionic liquids, dimer structures may provide some insight into the bulk liquid structure. The structures of 1-H,4-H-1,2,4-triazolium cation with dinitramide anion, and less thoroughly, 1-H,4-NH$_2$-1,2,4-triazolium cation (quaternized 4AT) with dinitramide will be considered here. Experimentally,[26] the former system is found to be a low melting salt (mp 75 °C), whereas the latter is a yellow oil (mp 20 °C). Unfortunately no crystal structure of the former system is available for comparison to the present results, but X-ray structures of similar materials suggest two possible types of ion interactions: coplanar or three-dimensional. Hydrogen bonding is the most important dimer interaction, and this will be maximized when the H-bond is linear. Examples of crystal structures showing
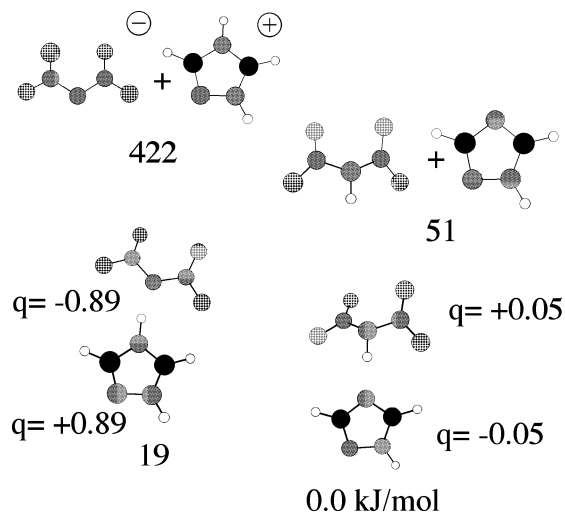

Figure 1. Relative energies (beneath each structure) of the most stable neutral dimer, and its corresponding ionic dimer. Structures, energies, and Mulliken charges are from RHF/6-31++G(d,p). As discussed in the text, the ionic dimer does not survive geometry optimization at the MP2 level.

coplanar interactions include the salts 1-H,3-N$_3$,4-H-1,2,4-triazolium nitrate[52] and 1-H,4-H-1,2,4-triazolium chloride.[80] Of course, solids contain more than just simple dimer interactions, and many body electrostatic forces may lead to more three-dimensional structures, in which as much H-bonding as possible is retained, while allowing ions to be surrounded by more oppositely charged ions. An example of this is 1-H,4-H-1,2,4-triazolium perchlorate[26] which contains some nearly linear NH–O interactions, but many more nearly perpendicular NH–O and CH–O interactions, resulting in a 3D lattice. A set of crystal structures[54] for doubly substituted triazoliums (organic groups at N_1 and amine at N_4) as bromide or nitrate salts have predominantly 3D organizations, controlled by hydrogen bonding between the amine and the anion.

As anticipated in the previous section, the lowest energy neutral (proton transferred) dimer is a hydrogen bonded system combining the lowest energy triazole with the lowest energy protonated dinitramide, shown in the lower right corner of Figure 1. The hydrogen bond/dipole interaction is fairly strong, so separating these neutral species from each other requires 51 kJ/mol. It is possible to locate ionic dimer structures at the Hartree–Fock level, and the corresponding ion dimer in Figure 1 lies 19 kJ/mol above the proton transferred neutral dimer. Of course, separating the ions to infinity requires a much larger energy than separating neutrals, 422 kJ/mol relative to the neutral pair. The similar magnitude of electrostatic stabilization that would result from bringing additional ions together (such as Alavi and Thompson[75] found for the ion tetramer $(NH_4^+)_2$-$(N(NO_2)_2^-)_2$) means that for triazolium based clusters with more than two ions, ionic structures can be presumed to lie below neutral structures. Figure 1 also contains an estimate of the charge separation, found by summing the Mulliken charges over all atoms in each ion at the RHF level, showing that the ionic structure is indeed quite ionic. MP2 single point calculations at the RHF geometry have a somewhat smaller Mulliken charge on the ions, ± 0.85 e$^-$.

Figures 2, 4, and 5 show that the triazolium/dinitramide system is very rich in both ionic and neutral structures. Figure 2 contains all ionic geometries found, which can transfer protons through the transition states shown in Figure 3, to yield the neutral structures given in Figure 4. The position of each dimer in Figures 2, 3, and 4 is kept consistent, so that any individual
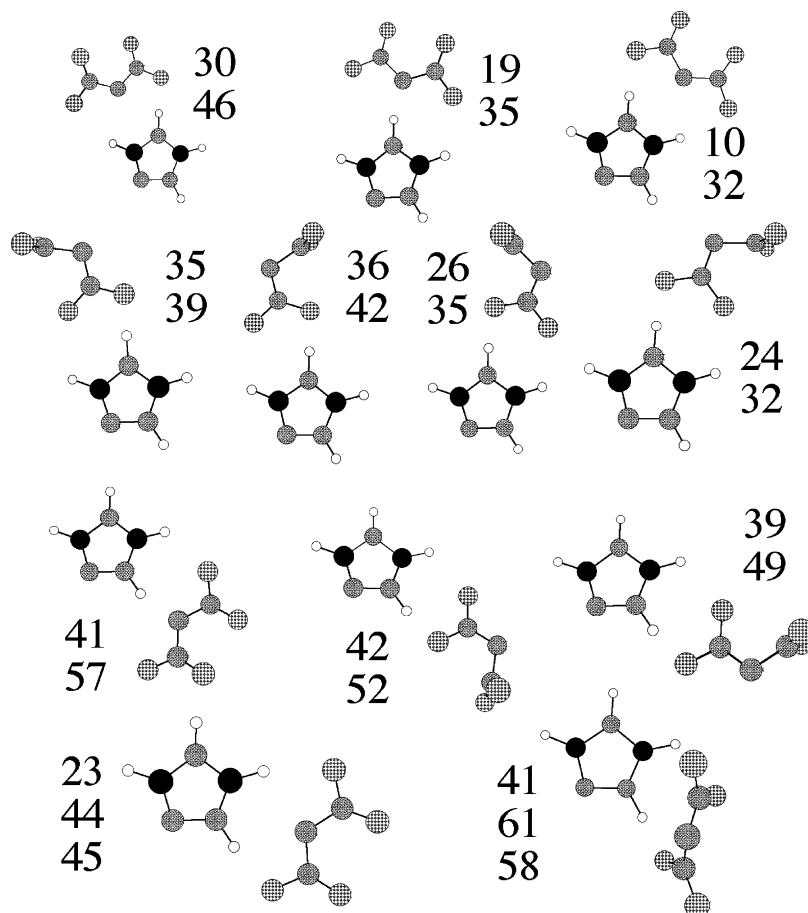
Figure 2. Ionic pairs in the parent 1,2,4-triazolium and dinitramide system, located at the RHF/6-31++G(d,p) level. The first and second energy values are from RHF/6-31++G(d,p) and MP2/6-31++G(d,p) at RHF geometries, in kJ/mol. The third value, if given, is at the fully optimized MP2/6-31++G(d,p) geometry. The zero of energy for Figures 2−6 is a neutral complex presented in Figure 4.

proton transfer reaction may be easily followed. The common zero of energy for all structures in Figures 2−5 is the most stable neutral dimer (already considered in detail in Figure 1), which can be found at the top center of Figure 4. Note that the orientation of the ring is kept the same in all geometries shown, so that the reader's eye can focus on the changing position of the dinitramide partner around the ring.

The top half of Figures 2 and 4 involves hydrogen bonding at the N_4 position of the ring, where the deprotonation of triazolium is easiest. The bottom half of these Figures gives H-bonded structures at N_1, where deprotonation is more difficult. Thus all energies in the bottom half of Figure 4 are higher than the top half. Within either half, the energy ordering can be rationalized by noting that the central N of dinitramide is the protonation site preferred over the terminal oxygens.

Figure 5 collects a few additional neutral structures in which the H atom in the protonated dinitramide is *not* hydrogen bonded to the triazole. Three of the five structures are nonplanar, and in fact, the stacked structure at the bottom right is found to exist only at the MP2 level. The bottom left figure has the central nitrogen of the dinitramide nearly coplanar with the ring, so its hydrogen is not participating in a hydrogen bond. Most of these have a rather high energy, and will not be considered further.

The minima presented in Figures 2 and 4 are mainly "coplanar", meaning that the three nitrogen atoms in the dinitramide moiety lie near the plane of the rings, although they are never precisely coplanar (structures have C_1, not C_s, symmetry). These structures were located by geometry optimization from 40 trial geometries, generated by placing the 5 possible pairs (dinitramide ion with triazolium ion, or either O

or N protonated dinitramide with either possible triazole) oriented with the three nitrogens perpendicular to the ring, in all 8 octants, about 7 Å from center to center. These 40 starting geometries were thus biased against the predominantly coplanar structures that result from geometry optimization, which are therefore clearly preferred by the hydrogen bonding contacts. After consideration of the results of these "random" geometry searches, additional, more rational searches were carried out. A total of 65 geometry searches for ionic or neutral pairs were performed, resulting in the 29 minima presented in Figures 2, 4, and 5. It is unlikely that all minima have been found! However, only one three-dimensional ion cluster and matching neutral complex was found, shown at the bottom right corner of Figures 2 and 4. One additional nonplanar minimum is not shown, namely a minimum similar to the 27 kJ/mol structure in Figure 4, in which the protonated dinitramide is rotated to be perpendicular to the triazole ring, at a relative energy of 31 kJ/mol (30 kJ/mol at the MP2 level). This structure was omitted because it appears to be just an internal rotational form of the planar structure depicted, as no such perpendicular ionic structure could be optimized.

MP2 energy computations at the RHF geometries give the second set of energy values given in Figures 2−5. Although 4 of the 11 ionic geometries given in Figure 2 have lower energies at the RHF level than their neutralized partners in Figure 4, MP2 computations preferentially stabilize the neutral forms, so all 11 ionic geometries lie higher in energy than their neutral forms. It may be seen by comparing Figure 2 to Figure 3 that although there are small barriers at the Hartree−Fock level for the proton transfer reactions that convert ionic pairs to neutral
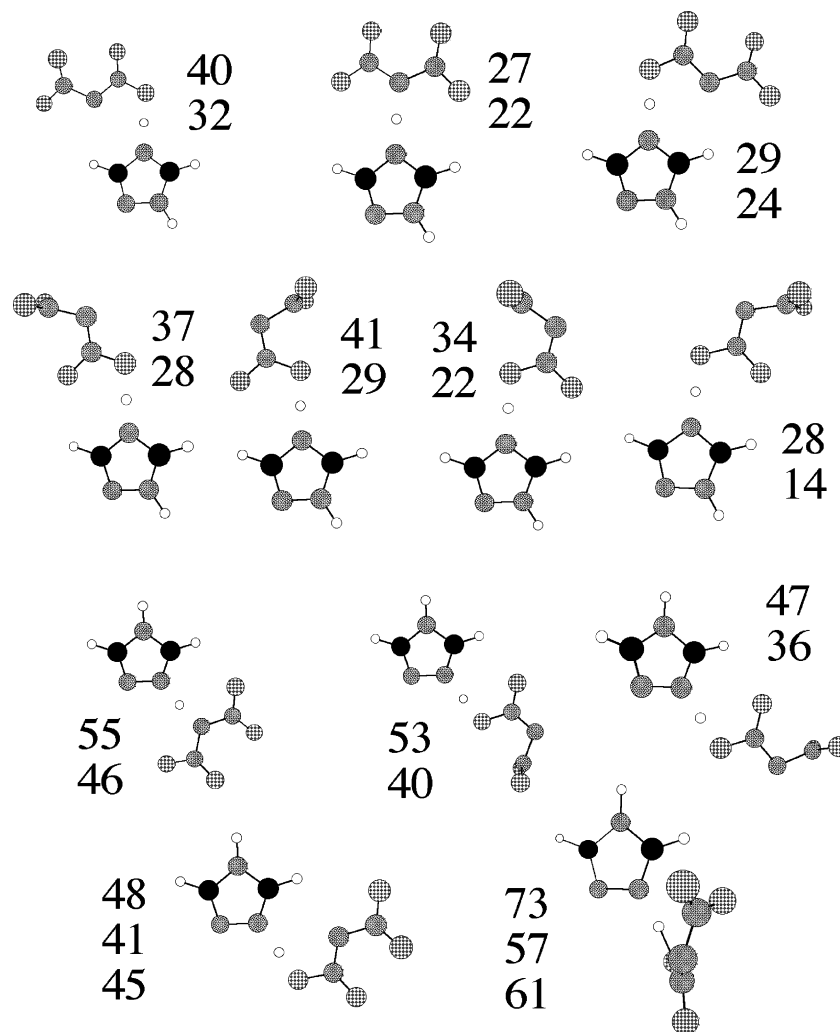
Figure 3. Transition states in the 1,2,4-triazolium and dinitramide system, connecting ionic pairs to neutral complexes. The three energy values have the same meaning as defined in Figure 2.

pairs (for example, a barrier of 8 kJ/mol for the most stable neutral dimer, featured in Figure 1), in all cases, the MP2 energies of the ionic forms in Figure 2 are slightly higher than those of the transition states in Figure 3. Therefore, nearly all structures given in Figure 2 are just shoulders on the MP2 potential surface, and MP2 geometry optimization leads to spontaneous proton transfers to structures such as those shown in Figure 4. However, the two ionic molecules in the bottom row of Figure 2 do possess shallow minima at the MP2 level. The third set of relative energies, where given, are MP2 energies at MP2 structures. Note that the MP2 barriers for proton transfers from the two stable ionic pairs are very small, just 0.6 and 2.8 kJ/mol.

Figure 6 contains the only dimer structure found for the 1,2 substituted triazolium ion. Figure 6 is actually part of the same potential energy surface as the structures in Figures 2−5, and is singled out only because it contains a 1,2 substituted triazolium. Both neutral and ionic structures are clearly energetically competitive, lying below many of the structures given in Figures 2−5. The 51 kJ/mol (see Figure 1) needed to separate the two monomers of the most stable neutral pair, followed by reattachment at N_2, is an upper limit on the energy required to access the neutral structure in Figure 6. Although the 1,2 substituted triazolium is more easily deprotonated than 1,4 substituted triazolium (see Table 6), an MP2 ionic minimum does exist, because the dinitramide is able to H-bond to both protons rather than just one in the 1,4 ionic complexes. Clearly

other neutral structures with hydrogen bonds between the ring N_2 and oxygen atoms in the dinitramide moiety may exist, at somewhat higher energy, but these were not searched for.

The available crystal structures[54] for bromide or nitrate salts of disubstituted triazoliums (N_1 organic, $N_4 = NH_2$) show three-dimensional structures resulting from H-bonding by the NH_2 groups. Accordingly, the results of a far less extensive search for ionic structures that might exist in the yellow oil, 1-H,4-NH_2-1,2,4-triazolium dinitramide is given here. The top part of Figure 7 shows the result of eight "random" searches as outlined above, with the two ions started about 7 Å apart, in all 8 octants. These searches did not lead to any minima involving hydrogen bonding at N_1 although clearly this search procedure is not exhaustive. Instead, the minima that were found show that hydrogen bonding at the amine group is quite favorable, accompanied by additional interactions between the ring and dinitramide. The existence of six such similar minima illustrates the large degree of flexibility in dinitramide ion. All six structures survive MP2 geometry optimization, which is not suprising because deprotonation at the amine would produce a zwitterion, not a neutral triazole. An explicit search for a structure with a dinitramide ion hydrogen bonded at its central nitrogen to the N_1 ring proton resulted in the location of a ionic minimum at the RHF level, shown in the lower left corner of Figure 7, at an energy comparable to the NH_2 bound structures. The previous section reported a slightly higher deprotonation energy for this ring proton (941 vs 927 kJ/mol in the parent),

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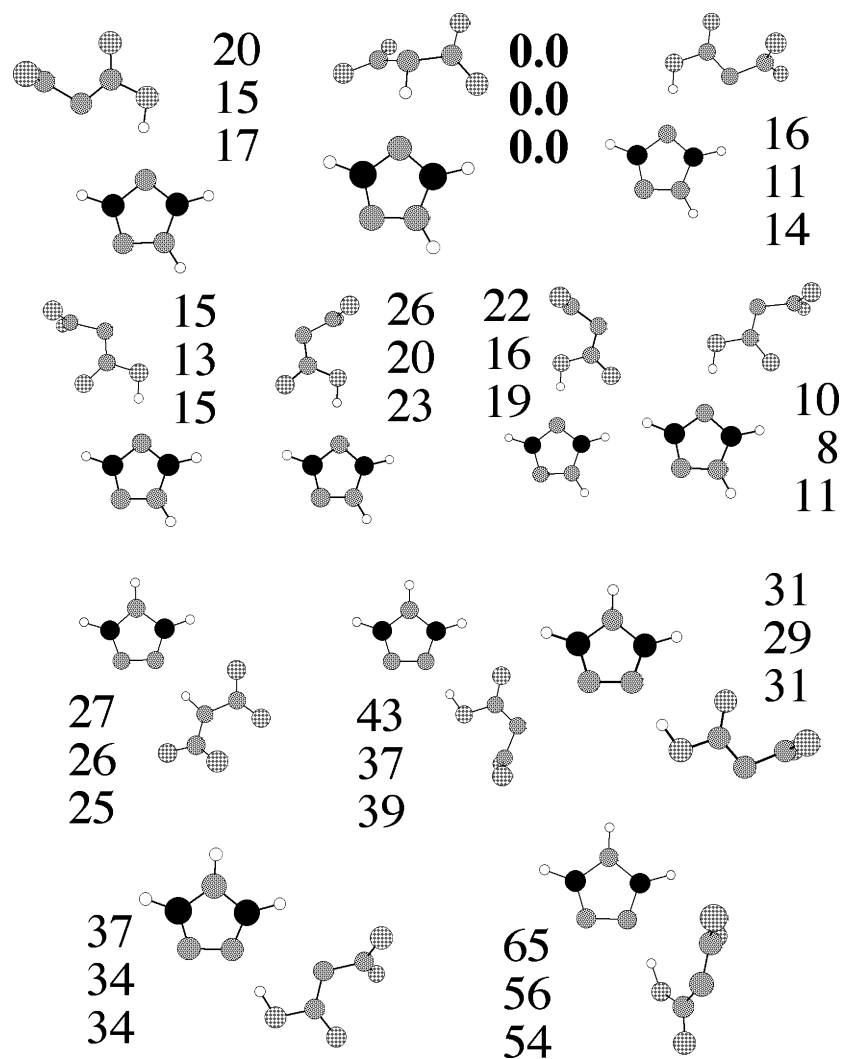*J. Phys. Chem. A, Vol. 109, No. 32, 2005* **7293**

Figure 4. Neutral dimers in the 1,2,4-triazolium and dinitramide system, resulting from proton transfers. The three energy values have the same meaning as defined in Figure 2. The lowest energy structure found is at the top center and is taken as the energy zero for Figures 2−6.
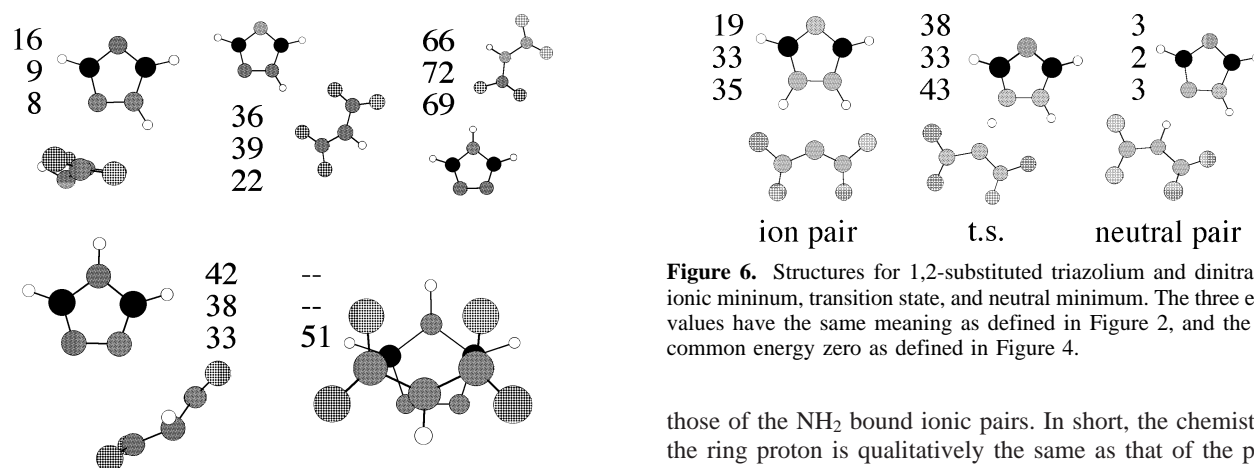

Figure 5. Additional neutral complexes, in which the dinitramide's H is not hydrogen bonded to the ring. The three energy values have the same meaning as defined in Figure 2.

and the RHF barrier seems more substantial than in the parent. Nonetheless, the MP2 energy at the RHF saddle point is already 11 kJ/mol below the MP2 single point energy of the ionic structure, and thus geometry optimization of this ionic structure leads to spontaneous proton transfer to the neutral pair in the lower right of Figure 7, whose energy is substantially below

ion pair   t.s.   neutral pair
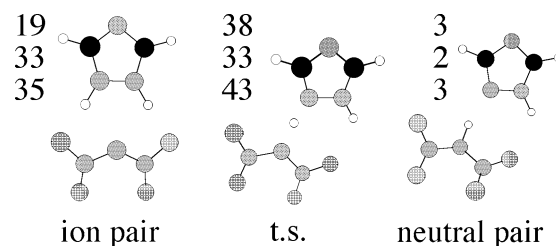
Figure 6. Structures for 1,2-substituted triazolium and dinitramide: ionic mininum, transition state, and neutral minimum. The three energy values have the same meaning as defined in Figure 2, and the same common energy zero as defined in Figure 4.

those of the NH_2 bound ionic pairs. In short, the chemistry of the ring proton is qualitatively the same as that of the parent triazolium, and the introduction of the amine changes the chemistry at N_4.

When combined with dinitramide anion, the unsubstituted 1-H,4-H-1,2,4-triazolium cation has a preference for coplanar geometries, whereas 1-H,4-NH_2-1,2,4-triazolium adopts more three-dimensional shapes. The amine group allows less ordered structures to exist, giving a plausible explanation for why the former system forms a low melting salt (mp 75 °C) but the latter is a yellow oil (mp 20 °C). Of course, an X-ray structure for the 1-H,4-H-1,2,4 triazolium dinitramide salt would be
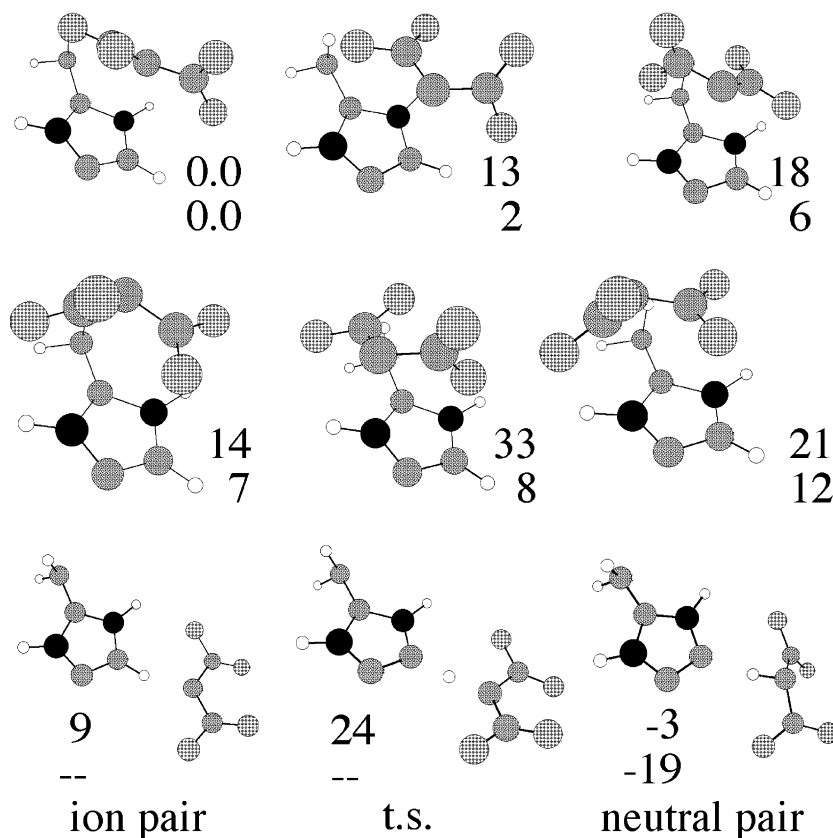
Figure 7. Structures for 1-hydro-4-amino-1,2,4 triazolium dinitramide. All but two of the structures shown are geometry optimized at the MP2/6-31++G(d,p) level, and possess positive definite Hessians at the RHF/6-31++G(d,p) level. The upper and lower energies are from RHF and MP2, respectively, in kJ/mol. The ionic structure and transition state in the bottom row are RHF/6-31++G(d) geometries.

welcome, to confirm whether the dimer geometries reported here are relevant in the bulk solid.

Summary

The results presented in this paper address several different aspects of energetic ionic liquids. The conclusions reached include the following:

1. The contribution of the two resonance structures in the unsubstituted triazolium cation is roughly equal, with approximately $3/2$ π electrons found on both charged nitrogens. Substitution at ring nitrogen atoms produces little change in the extent of this charge delocalization, as shown by both very small geometry changes in the rings, and by MCSCF analysis of the resonance hybrids. The two substituents that cause the most degradation to resonance are CN and NF_2, but to only a small extent. It appears that substitution will not hinder the ability of these cations to form ionic liquids.

2. A number of energetic and less energetic substituents at the ring nitrogens were investigated, and in all cases 1,4 substituted triazoliums are lower in energy than 1,2 substituted triazoliums. There is a small energy preference for monosubstitution at N_1 over N_4 in the 1,4 substituted triazoliums. The heats of formation for substituted gas-phase triazolium cations were presented, and the CN substituent is suggested as a synthetic target, over N_3, because the former does not require creating a ring *exo* NN bond, but rather a NC bond.

3. Triazolium dinitramide systems are rich in structure. The numerous geometries and their relative energies are understandable by consideration of hydrogen bonds and protonation energetics. The presence of only small energy barriers, or often, spontaneous transfer of protons from ionic dimers to produce

neutral pairs implies that deprotonation is a fundamental mechanism for triazolium decomposition.

The most important question that was not addressed in the present paper relates to the decomposition pathways of these energetic ionic liquids, beyond suggesting deprotonation as an initiating step. Little seems to be known about the decomposition of triazoles or triazolium ions, so experiments that detect products from their decomposition, or further theoretical work would be welcome. For example, would a triazole ring produced by deprotonation subsequently extrude molecular nitrogen? In contrast, a considerable amount of information about the decomposition of the dinitramide ion is available.[79]

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