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Inverse Sodium Hydride: A Theoretical Study

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Abstract: A recent experimental investigation in which a salt containing the unusual charge distribution H^+ and Na^- was synthesized and characterized prompted us to undertake an ab initio theoretical investigation. In the salt synthesized, the H^+ is bound to the nitrogen center of an amine and the Na^- alkali is “blocked” from approaching the protonated amine site by steric constraints of a cage structure. Although one expects that the Na^- would deprotonate an unprotected R_3N-H^+ cation, we decided to further explore this issue. Using extended atomic orbital basis sets and Møller–Plesset and coupled-cluster treatments of electron correlation, we examined the relative stabilities of the prototype $(Me)_3N + NaH$, $(Me)_3N + Na^+ + H^-$, $(Me)_3N-H^+ + Na^-$, and $(Me)_3N-Na^+ + H^-$ as well as the ion pair complexes $(Me)_3N-H^+ \cdots Na^-$ and $(Me)_3N-Na^+ \cdots H^-$. The primary focus of this effort was to determine whether the high-energy $(Me)_3N-H^+ \cdots Na^-$ ion pair, which is the analogue of what the earlier workers termed “inverse sodium hydride”, might be stable with respect to proton abstraction under any reasonable solvation conditions (which we treated within the polarized continuum model). Indeed, we find that such ion pairs are metastable (i.e., locally geometrically stable with a barrier to dissociation) for solvents having dielectric constants below ~ 2 but spontaneously decompose into their constituent ions for solvents with higher dielectric constants. We suggest that amines with large proton affinities and/or metals with weaker MH bond strengths should be explored experimentally.

I. Introduction

In a recent JACS communication,¹ the Dye group at Michigan State University reported the synthesis and characterization of an interesting crystalline salt in which sodium appears as the Na^- alkali anion and the counterion involves H^+ bound to a cage-protected amine, as shown in Figure 1.

As the authors of ref 1 explain, the importance of this salt lies in the fact that it contains sodium and hydrogen atoms in charge states that are opposite to those encountered in the usual NaH solid. That is, in NaH(s), one has Na^+ and H^- ions, whereas, in the new “inverse sodium hydride”, one finds Na^- and H^+ . This, in turn, is important because this charge distribution represents a high-energy state of NaH in which two electrons have migrated from the hydrogen center to the sodium. Clearly, one way new materials having high-energy content can be constructed is by using constituent “building blocks” that are in electronically excited states but that are metastable to spontaneous decay. The $Na^- + H^+$ ion pair is a simple, yet relevant, example that is studied in this work.

The key to being able to synthesize and isolate a stable salt in which sodium and hydrogen appear in their “inverse” charge states involved binding the H^+ to an amine in which the nitrogen

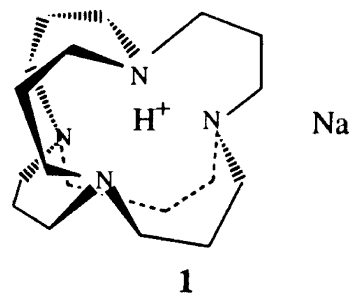


Figure 1. Structure of the ion pair appearing in the salt synthesized in ref 1.

centers are spatially isolated inside the 3^6 adamanzane (Adz) hydrocarbon cage, as shown in Figure 1. Doing so does not permit the alkali Na^- to approach the $-NH^+$ center closely enough to achieve proton abstraction



which could then lead to the much lower-energy Na^+H^- state. In earlier work by the Dye group,² it is made clear that it is expected that Na^- is able to abstract the proton from unprotected (i.e., in the absence of cage constraints) protonated amines, thus making the $Na^- \cdots H^+$ charge state impossible to maintain in the absence of such protection.

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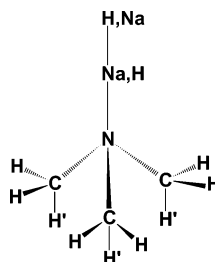
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Table 1. Bond Lengths (Å) and Angles (degrees) for Six Species^{a,b}

	$R(\text{C-N})$	$R(\text{C-H})$	$R(\text{C-H}')$	$R(\text{N-H})$	$R(\text{Na-H})$	$R(\text{Na-N})$		
I					1.920			
II	1.502	1.097	1.098	1.028				
III	1.482	1.099	1.099	1.119	2.585			
IV	1.462	1.101	1.115					
V	1.483	1.101	1.107			2.412		
VI	1.473	1.101	1.110		1.951	2.537		
	$\theta(\text{NCH}')$	$\theta(\text{NCH})$	$\theta(\text{H}'\text{CH})$	$\theta(\text{CNC})$	$\theta(\text{CNH})$	$\theta(\text{NHNa})$	$\theta(\text{CNNa})$	$\theta(\text{NNaH})$
II	107.866	108.806	110.390	111.336	107.535			
III	109.368	108.137	111.065	112.524	106.212	180.0		
IV	112.196	109.672	108.372	109.842				
V	111.047	109.974	108.278	108.333			110.586	
VI	111.510	109.788	108.469	109.110			109.830	180.0

^a I (NaH), II (Me₃NH⁺), III (Me₃NH⁺⋯Na[−]), IV (Me₃N), V (Me₃NNa⁺), VI (Me₃NNa⁺⋯H[−]). ^b Labeling of the H and H' atoms as shown below.



In the present effort, we examined the ground-state potential energy landscape of the prototypical *unprotected* system (Me)₃N + NaH as isolated (i.e., in the absence of solvent) species and in the presence of a range of solvation environments (described within the polarized continuum (PCM) model). Our goal was to examine the relative energies of (Me)₃N + NaH, (Me)₃N + Na⁺ + H[−], (Me)₃N–H⁺ + Na[−], (Me)₃N–Na⁺ + H[−] as well as the ion pair complexes (Me)₃N–H⁺⋯Na[−] and (Me)₃N–Na⁺⋯H[−] in an attempt to determine whether (Me)₃N–H⁺⋯Na[−] might be locally stable with respect to proton abstraction under any reasonable solvation conditions.

It turns out that our results indicate that solvent conditions may indeed be possible that would allow the “inverse” charge state ion pair to be locally geometrically stable, albeit still quite thermodynamically unstable, with respect to the much lower energy conventional charge state ion pair (Me)₃N–Na⁺⋯H[−]. Although our results, in particular those obtained with the PCM model of solvation, may not be accurate enough to make quantitative predictions, we believe that they suggest further experiments into the metastability of ion pairs such as (Me)₃N–H⁺⋯Na[−] should be undertaken.

II. Methods

The structures of the species (NaH, Me₃NH⁺, Me₃NH⁺⋯Na[−], Me₃Na⁺⋯H[−], Me₃N, Me₃NNa⁺) were optimized at the second-order Møller–Plesset perturbation theory level. The optimized geometries were then used to perform single-point energy calculations at higher orders of Møller–Plesset perturbation theory (MP_n; *n* = 2, 3, 4) and at the coupled cluster level with single and double excitations (CCSD) supplemented with a perturbational treatment of triple excitations (CCSD(T)).

The scans of the ground-state potential energy surface for the C_{3v} ion pair interactions, Na[−] + Me₃NH⁺ and H[−] + Me₃NNa⁺, were performed using second-order Møller–Plesset perturbation theory. To achieve a broader view of these reactions, we also studied the potential energy surface of the Me₃NH⁺⋯Na[−] complex for various NHNa angles and distances at the restricted Hartree–Fock (RHF) level and MP2 levels of theory. In all these calculations, we have used aug-cc-pVDZ

basis sets,³ because none of the ions involved has a diffuse enough charge density to require the use of extra diffuse functions. In other words, both H[−] and Na[−] bind their excess electron strongly (~0.7 eV) enough to not require special diffuse basis sets.

For studying our species in different solvents, we employed the polarized continuum model (PCM) of Tomasi and co-workers⁴ in which the solvent is modeled as a continuum, infinite, homogeneous, and isotropic dielectric medium, characterized by a dielectric constant ϵ . The molecule is placed into a cavity modeled on its real shape, and the electrostatic solute–solvent interactions are calculated by introducing an apparent surface charge distribution spread on the cavity surface. The PCM calculations in solvent were carried out with the same basis set as that for the isolated species. We computed single-point energies for the stationary points and transition state (TS) of our species at the CCSD(T) level.

In the present study, all our *ab initio* calculations were performed using the Gaussian 98 program⁵ on the Utah Center for High Performance Computing machines and our group’s AMD Athlon 2.0 GHz computers.

III. Findings

In Table 1, we give the geometrical parameters necessary to describe all of the species included in this study. In Figures 2–4 we detail how the ground-state energy of this system varies as a function of geometry with a goal of showing how the

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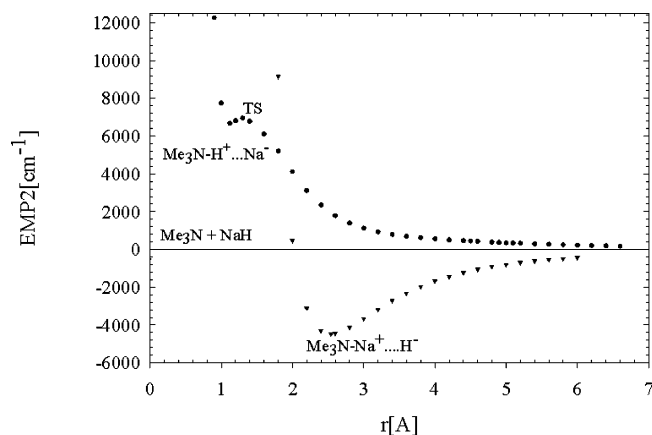


Figure 2. MP2 energies (cm^{-1}) connecting $\text{Me}_3\text{N} + \text{NaH}$ to (lower) the C_{3v} $\text{Me}_3\text{N}-\text{Na}^+\cdots\text{H}^-$ ion pair and to (upper) the C_{3v} $\text{Me}_3\text{N}-\text{H}^+\cdots\text{Na}^-$ ion pair. (●) $R(\text{H}-\text{N})$ in $\text{Na}^+\cdots\text{H}^+\cdots\text{N}(\text{CH}_3)_3$; (▼) $R(\text{Na}-\text{N})$ in $\text{H}^+\cdots\text{Na}^+\cdots\text{N}(\text{CH}_3)_3$.

species enumerated in Table 1 connect to one another. All of the energies shown in Figures 2–4 refer to “gas-phase” species (i.e., isolated species whose energies we computed in the absence of any solvation). These data serve as our reference point of what should be expected in the limit of an extremely weakly solvating environment.

In particular, Figure 2 shows how NaH and Me_3N (whose combined equilibrium MP2 and CCSD(T) energies, respectively, are $-336.341\,3292$ and $-336.429\,1409$ Hartrees) connect along two paths, both of which were obtained by varying the one geometrical parameter labeling the horizontal axis while minimizing the energy with respect to all other degrees of freedom.

1. Along the lower-energy path (where the $\text{Na}-\text{N}$ distance is scanned or varied), the Na center is directed toward the N atom of the amine to form the $\text{Me}_3\text{N}-\text{Na}^+\cdots\text{H}^-$ ion pair complex consisting of an Na^+ cation bound to the amine and an H^- anion bound to it.

2. Along the higher-energy path (where the $\text{N}-\text{H}$ distance is scanned), the H center is directed toward the N atom and forms the $\text{Me}_3\text{N}-\text{H}^+\cdots\text{Na}^-$ complex consisting of a protonated amine bound to the alkali Na^- .

To our surprise, the latter $\text{Me}_3\text{N}-\text{H}^+\cdots\text{Na}^-$ complex seems to be locally geometrically stable, as suggested by the small barrier in the upper curve in Figure 2 and the fact that it has all real harmonic vibrational frequencies. To further examine this possibility, we computed the energy of this system at a grid of distances ($R(\text{N}-\text{X})$ between the amine’s N atom and the midpoint of the $\text{Na}-\text{H}$ axis) and angles (between the $\text{Na}-\text{H}$ axis and the amine’s C_3 symmetry axis) with all other degrees of freedom optimized to minimize the energy. These data appear in Figure 3a–c. We also computed energies in the neighborhood of the $\text{Me}_3\text{N}-\text{H}^+\cdots\text{Na}^-$ ion pair and near the barrier at the CCSD(T) level to achieve our best estimates of these energies.

Figure 3a clearly shows (angle = 180°) the region of the $\text{Me}_3\text{N}-\text{Na}^+\cdots\text{H}^-$ minimum, which is labeled by an arrow. Figure 3b and c show the region (angle = 0°) near the protonated amine plus Na^- complex (again, located with an arrow) at two ranges of $R(\text{N}-\text{X})$. The presence of a local minimum near $R(\text{N}-\text{X}) = 2.4\text{ Å}$ and angle = 0° is clear, especially in Figure 3c. Finally, in Figure 4, we provide a contour plot of the same data shown in Figure 3c with the purpose of showing the radial and angular shape and depth of the minimum corresponding to

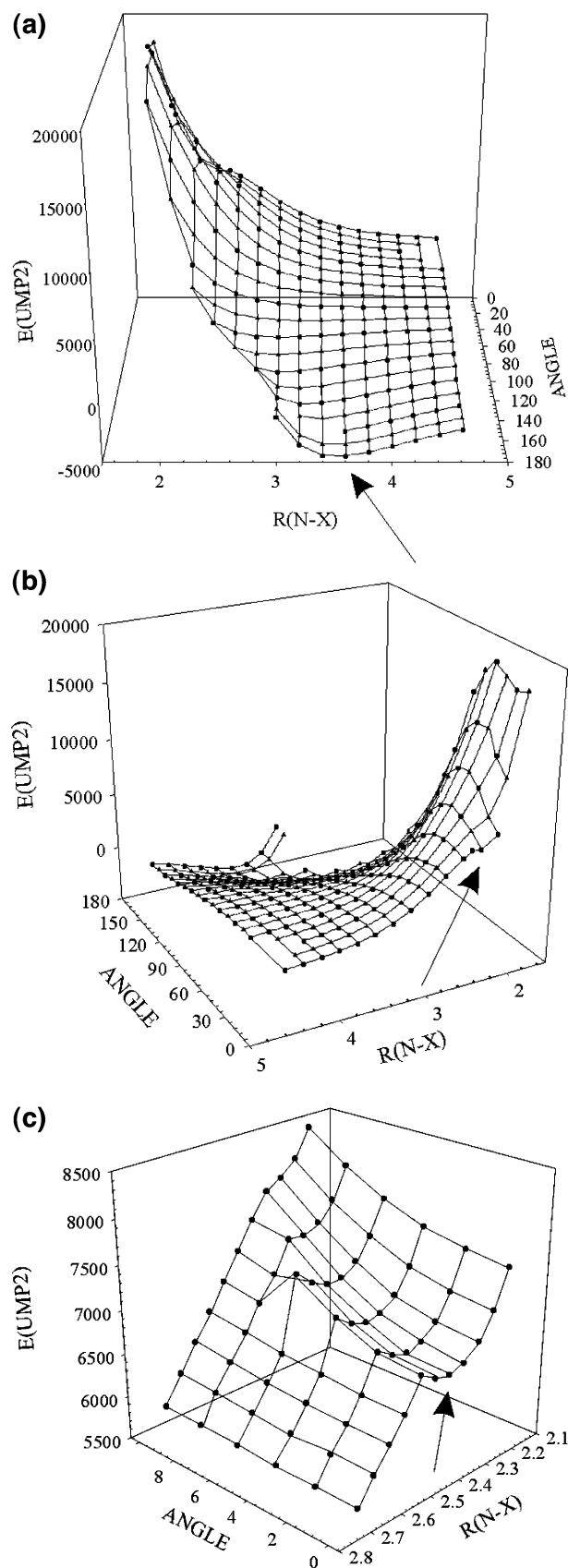


Figure 3. MP2 energies (cm^{-1}) for the $\text{Me}_3\text{N}-\text{Na}-\text{H}$ system as a function of the distance $R(\text{N}-\text{X})$ (Å) from N to the center of the $\text{Na}-\text{H}$ bond and the angle (degrees) between Me_3N ’s C_{3v} axis and the $\text{Na}-\text{H}$ internuclear axis. (a) View shows the $\text{Me}_3\text{N}-\text{Na}^+\cdots\text{H}^-$ minimum where the arrow points; (b) view shows the $\text{Me}_3\text{N}-\text{H}^+\cdots\text{Na}^-$ local minimum (arrow) and the transition state; (c) view is a more narrowly focused version of view b.

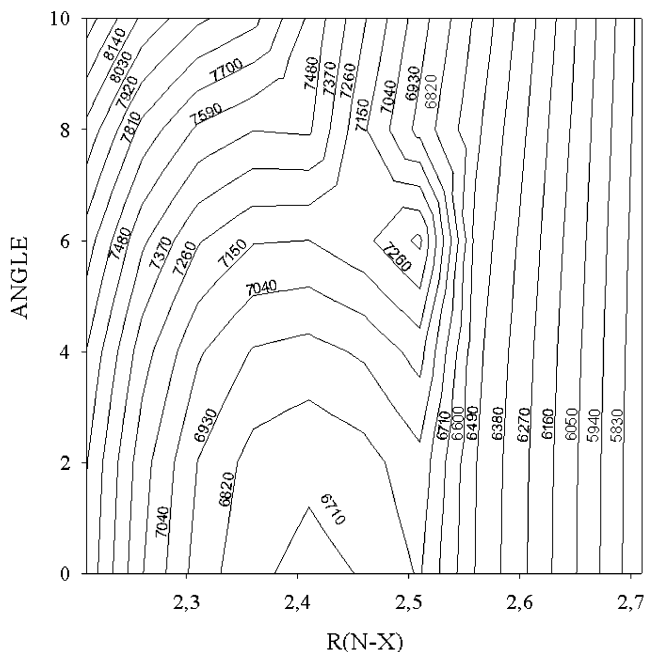


Figure 4. Contour plot of MP2 energies (cm^{-1}) in the region of the $\text{Me}_3\text{N}-\text{H}^+\cdots\text{Na}^-$ local minimum and the transition state.

the $\text{Me}_3\text{N}-\text{NH}^+\cdots\text{Na}^-$ complex near $\theta = 0^\circ$ and $R_{\text{NX}} = 2.4$ Å. The transition state appears near $R_{\text{NX}} = 2.5$ Å. It is this minimum and its potential survival under laboratory-achievable solvation conditions that intrigued us.

As Figures 2–4 illustrate, the $\text{Me}_3\text{N}-\text{H}^+\cdots\text{Na}^-$ minimum seems to (a) lie $\sim 6700 \text{ cm}^{-1}$ above the $\text{Me}_3\text{N} + \text{NaH}$ asymptote, which serves as the reference point (i.e., zero of energy) for all energies shown in this paper; (b) have a restoring force for bending (corresponding to a harmonic vibrational frequency of $\sim 145 \text{ cm}^{-1}$); and (c) have a barrier of $\sim 700 \text{ cm}^{-1}$ (computed at the CCSD(T) level for optimal accuracy) that renders it locally stable with respect to $\text{Me}_3\text{N} + \text{NaH}$.

After more carefully locating the $\text{Me}_3\text{N}-\text{Na}^+\cdots\text{H}^-$ local minimum and the transition state (TS) connecting it to $\text{Me}_3\text{N} + \text{NaH}$ at the CCSD(T) level, we carried out the series of CCSD(T) single-point energy calculations detailed in section II for a variety of solvation environments using the PCM model. Our findings are summarized in Figure 5, where the energies of the following species are shown: (a) the protonated amine $\text{Me}_3\text{N}-\text{H}^+$ and the Na^- anion (separated from one another); (b) the $\text{Me}_3\text{N}-\text{H}^+\cdots\text{Na}^-$ ion pair complex whose stability is our focal point; (c) the transition state connecting this ion pair to the $\text{Me}_3\text{N} + \text{NaH}$ fragments; (d) the lower-energy $\text{Me}_3\text{N}-\text{Na}^+\cdots\text{H}^-$ ion pair; and (e) the amine Me_3N plus $\text{Na}^+ + \text{H}^-$ (all separated from one another).

As noted previously, the common reference (i.e., $E = 0$) of energy for all of these data is the energy of the amine plus NaH in the absence of any solvation, so the energies shown in Figure 5 can be compared to those shown in Figures 2–4.

Two trends are worth noting in Figure 5: (1) As shown in the first and fifth columns, the separated-ion cases $\text{Me}_3\text{N} + \text{Na}^+ + \text{H}^-$ and $\text{Me}_3\text{N}-\text{H}^+ + \text{Na}^-$ clearly are least stable in the absence of solvent and most stable in water, our “strongest” solvent. (2) The ion pair complexes $\text{Me}_3\text{N}-\text{Na}^+\cdots\text{H}^-$ and $\text{Me}_3\text{N}-\text{H}^+\cdots\text{Na}^-$ have stability orderings as the solvent is varied approximately in the reverse order to those of the separated ions.

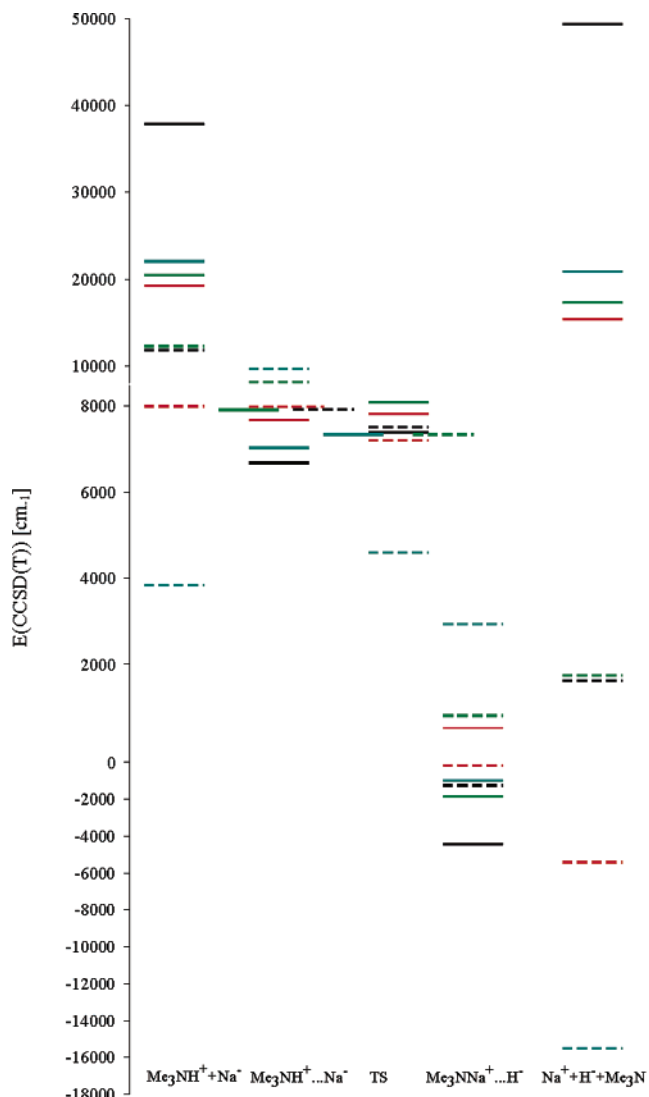


Figure 5. CCSD(T) energies (cm^{-1}) of species studied in this work for unsolvated (black line), chloroform (black dashed line), heptane (blue line), water (dashed blue line), toluene (red line), dichloroethane (red dashed line), carbontetrachloride (green line), diethylether (green dashed line).

These trends are, of course, not surprising and simply reflect stronger solvents’ ability to preferentially solvate the separated ions.

Most importantly, for only four cases (no solvent shown in black, heptane (with dielectric constant $\epsilon = 1.92$) in solid blue, toluene ($\epsilon = 2.38$) in solid red, and carbontetrachloride ($\epsilon = 2.23$) in solid green) is there a barrier separating the high-energy ion pair $\text{Me}_3\text{N}-\text{H}^+\cdots\text{Na}^-$ (second column in Figure 5) from the $\text{Me}_3\text{N} + \text{NaH}$.

These data suggest that it may be possible, in solvents with low dielectric constants, to form metastable protonated amine·alkalide ion pairs. Of course, it remains a significant laboratory challenge to find such a solvent that will also produce sufficient solubility for the “inverse” charge state’s ion pair as well as for precursor reagents. Moreover, it may be difficult, if not impossible, to use the specific amine and alkalide whose properties are studied here because of the very small ($\sim 700 \text{ cm}^{-1}$) barrier to reaction of the $\text{Me}_3\text{N}-\text{H}^+\cdots\text{Na}^-$ ion pair to produce $\text{Me}_3\text{N} + \text{NaH}$. However, by using an amine with a larger proton affinity⁶ (PA) and/or an alkali metal with a weaker

M–H bond strength,⁷ one may be able to achieve an $R_3N-H^+ \cdots M^-$ ion pair that is more stable and has a larger barrier to deprotonation. For these reasons, we believe that the findings presented here are sufficiently promising to prompt the laboratory chemists to look further into these issues.

IV. Summary

The results of our ab initio electronic structure study of the high-energy $(Me)_3N-H^+ \cdots Na^-$ ion pair (the analogue of what the workers termed “inverse sodium hydride”) may indeed be metastable with respect to proton abstraction (i.e., locally geometrically stable with a barrier to dissociation) for solvents having dielectric constants below ~ 2 . In contrast, such ion pairs are predicted to spontaneously decompose into $Me_3N + NaH$, which then yields $Me_3N + Na^+ + H^-$ in solvents with higher dielectric constants. Because such inverse charge state species lie at high energies, our data suggest the need for further

experimental study of the possibility that unprotected protonated amines complexed with alkalides may be synthesized under proper solvent conditions. In addition, we suggest that using amines with larger proton affinities and/or alkali metals with weaker M–H bond strengths may allow one to achieve an $R_3N-H^+ \cdots M^-$ ion pair that is more stable and has a larger barrier to dissociation.

Finally, we should note that, even at the equilibrium geometry of the $Me_3N-H^+ \cdots Na^-$ complex, promotion of a single electron to yield $Me_3N-H \cdots Na$ is not energetically favored. Thus, the $Me_3N-H^+ \cdots Na^-$ complex seems to be electronically stable with respect to a rearrangement of the electronic orbital occupancy that might be expected to lead to fragmentation (since Me_3N-H neutrals are known to be geometrically unstable).

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(6) Me_3N has a proton affinity (PA) of 225 kcal mol⁻¹, which is quite large; other amines include Me_2NH (220 kcal mol⁻¹), $EtNH_2$ (217 kcal mol⁻¹), $phenyl-NH_2$ (209 kcal mol⁻¹), FNH_2 (188 kcal mol⁻¹), and NH_3 (204 kcal mol⁻¹). Amines with larger PAs include quinoline (228 kcal mol⁻¹), 2,6-dimethyl pyridine (230 kcal mol⁻¹), and Bu_2NH .

(7) NaH has a bond energy of ~ 2.2 eV.; others include LiH (2.5 eV), KH (1.8 eV), and RbH (1.9 eV).