Factors That Influence the C═N Stretching Frequency in Imines

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The factors that influence the C═N stretching frequency and the C═N π-bond strength of unprotonated and protonated imines have been studied using generalized valence bond (GVB) calculations. For simple imines, such as, CH_2═NH and *trans*-CH_3CH═NCH_3, the C═N stretching force constant increases upon protonation, whereas for polyimines (CH_2═(CHCH═)$_n$NH), the C═N stretching force constant decreases by 0.47 mdyn/Å upon protonation. The calculations clearly show that the C═N(H) stretching frequency and its deuterium isotope shift in protonated imines are significantly influenced by the C═NH bending and the C═N/C═NH coupling force constants. The increase in the C═N(H) stretching frequency upon protonation is shown to be neither due to a negative C═N/C═NH coupling force constant nor due to the C═N stretching but to be mainly due to the strong contribution from the large C═NH bending force constant (1.08 mdyn/rad^2) and a positive coupling constant (0.30 mdyn/rad). This C═NH bending contribution also affects the C═N(H) stretching frequency deuterium isotope shift. The GVB calculations predict a deuterium isotope shift of 26 cm^{-1} in the C═N(H) stretching frequency and a ^{15}N isotope shift of 18 cm^{-1}, which are in excellent agreement with the corresponding experimental values of 25 and 15 cm^{-1}, respectively.

I. Introduction

The imine (C═N) linkage has attracted much interest because of its occurrence in the visual pigment rhodopsin and bacteriorhodopsin.[1] Since the C═N linkage is versatile in its physical and chemical properties, imines play an important role in biological catalysis. The C═N bond is labile and can be hydrolyzed and re-formed readily.

Protonation of the nitrogen of an imine containing chromophore generally leads to a marked red shift in the chromophore absorption spectrum. This reaction is important in controlling the optical properties of retinal in the visual pigment rhodopsin. Many spectroscopic studies and theoretical calculations[2] have been carried out to try to understand the chromophore absorption spectrum of rhodopsin.

Protonation of an imine, or reaction with Lewis acids, usually results in an increase in the C═N stretching frequency.[3] Changes in the C═N stretching frequency in deuterated solutions have been regarded as the most reliable measure of whether or not the imine is protonated.[4] For instance, Raman[5a−c] and IR spectroscopic[5d,13] studies have shown that rhodopsin has a C═N stretching frequency of 1660 cm^{-1} and an unusually large deuterium shift of ~25 cm^{-1}.[5] The large deuterium shift in the C═N(H/D) stretching frequency suggests that the imine nitrogen in rhodopsin is strongly hydrogen bonded. The C═N stretching frequency is often used as a measure of π-electron distribution in the imine region of the molecule. Being a reactive part of the chromophore, chemical modification of the protein and chromophore makes it possible to study the C═N bond in considerable detail. An accurate understanding of the factors that determine the C═N stretching frequency is therefore clearly needed. Methylimine (CH_2═NH), the simplest imine, and its protonated derivative serve as model systems that can be used to study the electronic charge distribution in the C═N bonding region. A number of ab initio calculations of the force field of methylimine have been carried out.[6,7] The PRDDO and HF calculations by Eades et al.[6] predict an increase in the C═N bond length of 0.02 Å upon protonation. They also obtained the vibrational frequencies for unprotonated and protonated methylimines. In contrast to the calculations of Eades et al., Harrison et al.'s GVB calculations[7] showed a slight decrease in the C═N bond length and an increase of 0.51 mdyn/Å in the C═N force constant upon protonation. Harrison et al. also examined the frequency changes for *N*-ethylidenemethylamine (CH_3CH═NCH_3)[3] using the empirical force field constructed from their GVB methylimine geometry and force constants. The study showed that an increase in the C═N stretching force constant (by 0.51 mdyn/Å) upon protonation translates into a corresponding increase in the C═N stretching frequency of ~30 cm^{-1}.

Protonation of a polyimine, however, results in a decrease in the π bond order and a corresponding decrease in the C═N force constant. Empirical force field calculations[8,9] have found that the coupling between the C═N stretching and the C═NH bending modes makes an important contribution to the C═N stretching frequency and pushes it to the higher frequencies observed experimentally. A normal coordinate analysis of the model aromatic imine *trans-N*-benzylideneaniline (tBA) using the AM1 method obtained a decrease in the C═N stretching force constant but an increase of 45 cm^{-1} in the C═N stretching frequency.[10] Ab initio HF calculations on polyimines have shown that protonation causes a charge alternation in the chain along with conjugation at the C═NH_2^+ end of the molecule.[11,12] Recently, based on HF and MP2 calculations of the force field for protonated and unprotonated imines,[28] it has been concluded that at least MP2 level is necessary for correctly calculating C═N frequency shifts upon protonation. To obtain a better understanding of the changes that occur in imines upon protonation, GVB calculations of the force field for a number of imines have been carried out. In this study, accurate force fields for unprotonated and protonated CH_2═NH and *trans*-CH_3CH═NCH_3 were calculated at the GVB(6/12)/6-31G* level. The frequencies were then calculated to investigate whether the C═NH bending motion makes an important contribution to the C═N stretching frequency shift. The change in the C═N π

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bond energy upon protonation was studied by calculating the barrier to rotation around the C=N double bond. GVB equilibrium geometries were also obtained for polyimines to determine the effect of conjugation on the C=N bond length, force constants, rotation barrier, and charge distribution.

II. Computational Method

The calculations were carried out with our recently developed GVB program[14] which is part of the ab initio package MUNGAUSS.[15] MUNGAUSS is written using the OSIPE (open structured interfaceable programming environment) tools, which is an "object-oriented" approach to programming in which objects are computed dynamically.[16] The GVB perfect-pairing (GVB-PP) orbitals can be generated automatically (for specific bonds or electron pairs) by using Boys' localized (extended Hückel or Hartree−Fock) molecular orbitals (LMOs). The GVB program also has a number of developments which give excellent convergence. With this approach, selecting the perfect-pairing orbitals associated with the A−B bond is straightforward. The resulting GVB pair function ψ_{A-B} corresponding to the A−B bond can be constructed using the following pairing orbitals:

$$\psi_{A-B} = (\sigma_i \psi_i^{LMO} \psi_i^{LMO} - \sigma_j \psi_j^{LMO} \psi_j^{LMO})(\alpha\beta - \beta\alpha) \qquad (1)$$

where σ_i and σ_j ($\sigma_i^2 + \sigma_j^2 = 1$) are referred as to the GVB CI coefficients, and ψ_i^{LMO} and ψ_j^{LMO} are bonding and antibonding molecular orbitals, respectively.

In this study, GVB calculations were carried out using 12 PP orbitals for six pairs of electrons, GVB(6/12). The GVB(6/12) wave function includes the C−N σ and π bonds, two C−H bonds, one N−H bond, and one nitrogen lone pair for the unprotonated imines, which is replaced by one N−H bond for the protonated imines, *i.e.*,

$$\Psi^{GVB}_{(unprotonated)} = A[\Psi_{core}\psi_{C-N(\sigma)}\psi_{C-N(\pi)}\psi_{C-H1}\psi_{C-H2}\psi_{N-H}\psi_{N-1p}]$$

$$\Psi^{GVB}_{(protonated)} = A[\psi_{core}\psi_{C-N(\sigma)}\psi_{C-N(\pi)}\psi_{C-H1}\psi_{C-H2}\psi_{N-H1}\psi_{N-H2}] \qquad (2)$$

where A is the antisymmetrizer, Ψ_{core} is the core wave function, and ψ_{N-H}, ψ_{N-1p}, ..., are the GVB pair functions defined by eq 1. All the GVB(6/12) calculations were performed using the 6-31G* basis set and are denoted as GVB(6/12)/6-31G*. The equilibrium structures were optimized using Davidon's OC gradient method.[17] Transition state structures were optimized using a minimization of the sum of squares of gradient method[18] and were characterized to have only one imaginary frequency. The GVB(6/12)/6-31G* force constants were calculated numerically.[19] A modified BEBOVIB-VI program[20] was used to calculate the normal coordinate vibrational frequencies. The HF and MP2 vibrational frequencies were calculated using scaled (0.9) force constants, but the GVB frequencies reported here are unscaled.

III. Results and Discussion

1. Changes in the C=N Bond Length upon Protonation. Optimized GVB(6/12)/6-31G* geometries were obtained for the unprotonated and protonated imines. The C=N bond lengths are given in Table 1 along with values from other ab initio calculations. The GVB(6/12)/6-31G* C=N bond length for methylimine (1.282 Å) is closer to the experimental value (1.273 Å),[27] compared with the previous results, *e.g.*, 1.257 Å (HF)[6] and 1.289 Å (GVB).[7] At the PRDDO and HF level,[6] protonation results in an increase in the C=N bond of 0.02 Å, while the previous GVB calculations predicted a small decrease of 0.007 Å. Our GVB(6/12)/6-31G* calculations also predict a similar but smaller decrease of only 0.001 Å after protonation. Upon protonation, the C−N−H bond angle changes from 110.5° (sp^3) to 121.9° (sp^2), and the N−H bond length is shorter by 0.005 Å. For *trans*-$CH_3CH{=}NCH_3$, the methyl substituents result in a slightly shorter C=N bond length (1.278 Å) than that in methylimine but a slightly longer C=N bond length (1.285 Å) for the protonated case.

TABLE 1: Effect of Protonation on the C=N Bond Length (Å) of Imines[a]

compd	C=N	C=NH$^+$
$H_2C{=}NH$ (this work)	1.282	1.281
GVB[3,7]	1.289	1.282
PRDDO[6]	1.262	1.281
HF/DZD[6]	1.257	1.272
$CH_3CH{=}NCH_3$ (this work)	1.278	1.285
GVB[3,7]	1.289	1.281
$H_2C{=}(CHCH{=})_1NH$	1.284	1.295
$H_2C{=}(CHCH{=})_2NH$	1.284	1.303
$H_2C{=}(CHCH{=})_3NH$	1.285	1.307
$H_2C{=}(CHCH{=})_6NH$	1.284	1.306

[a] C=N for unprotonated, C=NH$^+$ for protonated.

TABLE 2: Effect of Protonation on the Force Constants of Imines[a]

imine	C=N stretch[b]	C=N(H$^+$) stretch[b]	C=NH bend[c]	C=N/C=NH coupling[d]
$H_2C{=}NH$ (this work)	10.48	11.18	1.06	0.33
GVB[7]	11.14	11.65		
HF[7]	13.77	13.25		
$CH_3CH{=}NCH_3$ (this work)	10.61	10.85	1.20	0.30
ref 3	10.60	11.10		
$H_2C{=}(CHCH{=})_1NH$	10.38	10.20	1.12	0.31
$H_2C{=}(CHCH{=})_2NH$	10.19	9.82	1.08	0.31
$H_2C{=}(CHCH{=})_3NH$	10.17	9.70	1.08	0.31
$H_2C{=}(CHCH{=})_6NH$	10.16	9.68	1.08	0.31

[a] C=N for unprotonated, C=NH$^+$ for protonated. [b] In mdyn/Å. [c] In mdyn/rad^2. [d] In mdyn/rad.

Compared with the early HF/STO-3G results by Poirier et al.,[22] the GVB(6/12)/6-31G*-optimized geometries for the polyimines have much shorter bond lengths, especially in the C=N bonding region. Protonation causes a similar increase in conjugation along the chain, which is reflected by the equalization of the single and double C−C bond lengths. The GVB(6/12)/6-31G*-optimized C=N bond lengths, for both the unprotonated and protonated polyimines, $CH_2{=}(CHCH{=})_nNH$ (n = 0, 1, 2, 3, and 6), are given in Table 1. In going from methylimine ($n = 0$) to the simplest polyimine ($n = 1$), the C=N bond distance increases by 0.002 Å for the unprotonated imine and increases by 0.014 Å for the protonated imines. The increase in the C=N bond length is significantly larger in the protonated imine. For the unprotonated imines with $n = 1$ to $n = 6$, the C=N bond length is essentially constant. On the other hand, for the protonated case, the C=N bond length increases from $n = 0$ to $n = 3$, in agreement with previous results.[22] Therefore, the change in the C=N bond length upon protonation increases with chain length, from −0.001 to +0.022 Å, for $n = 0$ to $n = 3$, and remains constant from thereon.

2. Force Constants. The calculated force constants for protonated and unprotonated imines are given in Table 2. For methylimine, the GVB(6/12)/6-31G* C=N stretching force constants are slightly smaller than previous GVB values and much smaller than the previous HF values for both the

TABLE 3: Comparison of Calculated Frequencies (cm^{-1}) for $\mathrm{H_2C{=}NH}$

vib modes	HF/ 6-31G*[21]	MP2/ 6-31G*[21]	GVB(6/12)/ 6-31G* (this work)	exptl[27]
NH stretch (a′)	3347	3291	3254	3297
$\mathrm{CH_2}$ s stretch (a′)	3012	3091	3018	3036
$\mathrm{CH_2}$ a stretch (a′)	2929	2960	2935	2924
CN stretch (a′)	1719	1638	1628	1640
in-plane bend (a′)	1465	1448	1453	1453
in-plane bend (a′)	1346	1341	1372	1347
torsion (a″)	1143	1101	1133	1123
out-of-plane bend (a″)	1048	1052	1050	1069
in-plane bend (a′)	1011	1045	979.4	1059

unprotonated and protonated cases.[7] GVB(6/12)/6-31G* predicts an increase of 0.70 mdyn/Å in the $\mathrm{C{=}N}$ stretching force constant upon protonation, which is larger than the 0.51 mdyn/Å value obtained by Harrison et al.[7] Our GVB(6/12)/6-31G* $\mathrm{C{=}N}$ stretching/$\mathrm{C{=}NH}$ bending coupling force constant for protonated methylimine is 0.33 mdyn/rad (*cf.* Table 2).

For unprotonated and protonated *trans*-$\mathrm{CH_3CH{=}NCH_3}$, the MP2 $\mathrm{C{=}N}$ stretching force constants are predicted to be nearly equal.[28] The GVB(6/12)/6-31G* $\mathrm{C{=}N}$ stretching force constant for *trans*-$\mathrm{CH_3CH{=}NCH_3}$ is 10.61 mdyn/Å compared with 10.48 mdyn/Å value in methylimine due to a shorter bond distance (1.278 vs 1.282 Å). On the other hand, the $\mathrm{C{=}N}$ stretching force constant in protonated *trans*-$\mathrm{CH_3CH{=}NCH_3}$ (10.85 mdyn/Å) is smaller than in protonated methylimine (11.18 mdyn/Å), due to a slightly longer bond distance (1.285 vs 1.281 Å). Upon protonation, the $\mathrm{C{=}N}$ stretching force constant of *trans*-$\mathrm{CH_3CH{=}NCH_3}$ increases by 0.24 mdyn/Å, compared with the 0.51 mdyn/Å value used by Harrison et al. in their model calculations.[3] The GVB(6/12)/6-31G* calculations predict a large $\mathrm{C{=}NH}$ bending force constant of 1.20 mdyn/rad^2, with a strong $\mathrm{C{=}N}$/$\mathrm{C{=}NH}$ coupling of 0.30 mdyn/rad (*cf.* Table 2), for protonated *trans*-$\mathrm{CH_3CH{=}NCH_3}$. This $\mathrm{C{=}N}$/$\mathrm{C{=}NH}$ coupling is very close to the value obtained for protonated methylimine.

The calculated bond lengths and the force constants, for $n = 3$ and $n = 6$, are essentially identical (*cf.* Tables 1 and 2). Therefore, the simple polyimine, $\mathrm{H_2C{=}(CHCH{=})_3NH}$, is a good model for larger polyimines. The protonated imine $\mathrm{C{=}N}$ stretching force constant is 9.70 mdyn/Å, a decrease of 0.47 mdyn/Å upon protonation, instead of an increase as suggested by Harrison et al.[3] The GVB(6/12)/6-31G* $\mathrm{C{=}N}$ stretching force constants from this study are very close to the empirical values used by other workers,[9] providing a theoretical basis for those empirical values. However, the $\mathrm{C{=}N}$/$\mathrm{C{=}NH}$ coupling force constant is clearly not negative, as used in the previous empirical calculations,[8] but positive. A normal coordinate analysis of unprotonated, protonated, and deuterated imines is necessary to assign the $\mathrm{C{=}N}$ stretching mode and to understand the origin of the various frequency shifts.

3. Vibrational Frequencies and Their Isotopic Shifts. The results of our GVB optimized structures and the calculated force constants show that using the force constants and geometries of methylimine for other polyimines is evidently not appropriate. The GVB(6/12)/6-31G*-calculated force constants and normal coordinate frequencies with the different isotope effects are used to investigate the influence of protonation on the $\mathrm{C{=}N}$ stretching vibration. The calculated GVB(6/12)/6-31G* frequencies for methylimine are listed in Table 3, along with the experimental, HF/6-31G*, and MP2/6-31G* frequencies.[21] The GVB(6/12)/6-31G* frequencies are in reasonable agreement with the experimental values.[27] For example, the GVB(6/12)/6-31G* $\mathrm{C{=}N}$ stretching frequency of 1628 cm^{-1} is very close to the MP2/6-31G*[21] value of 1638 cm^{-1} and to the experimental frequency of 1640 cm^{-1}. The overestimation by HF of the $\mathrm{C{=}N}$ stretching frequency (1719 cm^{-1}) is partly due to an overestimation of the force constant and thus underestimation of the $\mathrm{C{=}N}$ bond distance. The GVB(6/12)/6-31G* $\mathrm{C{=}N}$ vibrational frequencies along with their isotopic shifts, for unprotonated and protonated methylimine, *trans*-$\mathrm{CH_3CH{=}NCH_3}$ and $\mathrm{H_2C{=}(CH\text{-}CH{=})_3NH}$, are listed in Table 4. The GVB(6/12)/6-31G* $\mathrm{C{=}N}$ stretching frequency of 1659 cm^{-1} for $\mathrm{H_2C{=}(CHCH{=})_3NH}$ is close to the previously calculated values of 1630[8a] and 1624 cm^{-1} [8b] and close to the experimental value of 1632 cm^{-1} [5,13] and similarly for the protonated imine (*cf.* Table 4). The calculated isotopic shifts for $\mathrm{H_2C{=}(CHCH{=})_3NH}$ are also in good agreement with experiment, 18 vs 15 cm^{-1} [23] for $\mathrm{^{14}N/^{15}N}$, 26 vs 25 cm^{-1} [5,13] for H/D, and 22 vs 28 cm^{-5} [1,13] for shifts due to protonation. The GVB(6/12)/6-31G* $\mathrm{C{=}N}$ stretching frequency deuterium isotope shift of 26 cm^{-1} is also in good agreement with the value of 28 cm^{-1} obtained by semiempirical force-field calculations for *all-trans* protonated imines.[2]

Except for the $\mathrm{^{13}C{=}NH^+}$ frequency, all the $\mathrm{C{=}N}$ stretching frequencies increase in going from methylimine to *trans*-$\mathrm{CH_3CH{=}NCH_3}$. On the other hand, the $\mathrm{C{=}N}$ stretching frequency increases from methylimine to $\mathrm{H_2C{=}(CHCH{=})_3NH}$ for the unprotonated case but decreases for the protonated case. This is primarily due to the substantial increase in the $\mathrm{C{=}N}$ bond length upon protonation of the polyimines.[22] In all three cases, protonation increases the $\mathrm{C{=}N}$ stretching frequency, methylimine having the largest increase, 110 cm^{-1} compared with 58 cm^{-1} for *trans*-$\mathrm{CH_3CH{=}NCH_3}$ and only 22 cm^{-1} for $\mathrm{H_2C{=}(CHCH{=})_3NH}$. Methylimine, *trans*-$\mathrm{CH_3CH{=}NCH_3}$, and

TABLE 4: Calculated $\mathrm{C{=}N}$ Stretching Frequencies and Isotopic Shifts (cm^{-1})

vib mode	$\mathrm{H_2C{=}NH}$	$\mathrm{CH_3CH{=}NCH_3}$	$\mathrm{H_2C{=}(CHCH{=})_3NH}$[a]
$\mathrm{C{=}N}$	1628	1688	1659 (1632,[b] 1630,[c] 1624[d])
$\mathrm{C{=}^{15}N}$	1614	1668	1641
$\mathrm{C{=}(^{14}N/^{15}N)}$ shift	14	20	18 (15[e])
$\mathrm{^{13}C{=}N}$	1597	1653	1625
$\mathrm{(^{12}C/^{13}C){=}N}$ shift	31	35	34
$\mathrm{DC{=}N}$	1585	1669	1640
$\mathrm{(H/D)C{=}N}$ shift	43	19	19
$\mathrm{C{=}NH^+}$	1738	1746	1681 (1660,[b] 1659,[c] 1658[d])
$\mathrm{C{=}N/C{=}NH^+}$ shift	110	58	22 (28,[b] 29,[c] 34[d])
$\mathrm{C{=}ND^+}$	1685	1726	1655 (1635,[b] 1633,[c] 1625[d])
$\mathrm{C{=}N(H/D)^+}$ shift	53	20	26 (25,[b] 26,[c] 33[d])
$\mathrm{^{13}C{=}NH^+}$	1723	1718	1655
$\mathrm{(^{12}C/^{13}C){=}NH^+}$ shift	15	28	26
$\mathrm{DC{=}NH^+}$	1721	1732	1665
$\mathrm{(H/D)C{=}NH^+}$ shift	17	14	16

[a] The values in parentheses are for more complex polyimines. [b] Experimental data.[5,13] [c] Empirical calculations from Honig et al.[8a] [d] Empirical calculations from Callender et al.[8b] [e] Experimental data.[23]

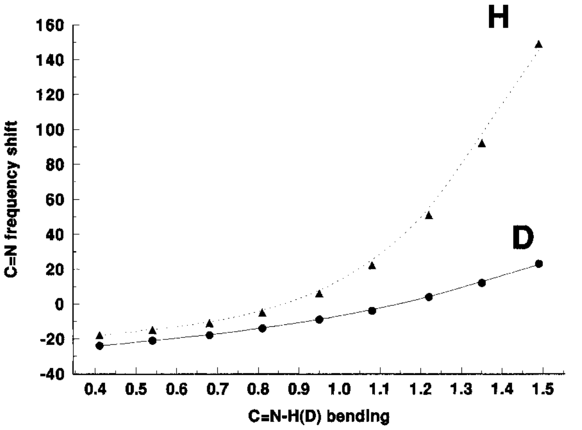

Figure 1. Shift in the C=N stretching frequency ($\nu_{C=N(H)} - \nu_{C=N}$, and $\nu_{C=N(D)} - \nu_{C=N}$) due to protonation of $H_2C{=}(CHCH{=})_3NH$ as a function of C=NH bending force constant. The coupling force constant is kept constant at 0.31 mdyn/rad. The triangle is for C=NH and the circle for C=ND.

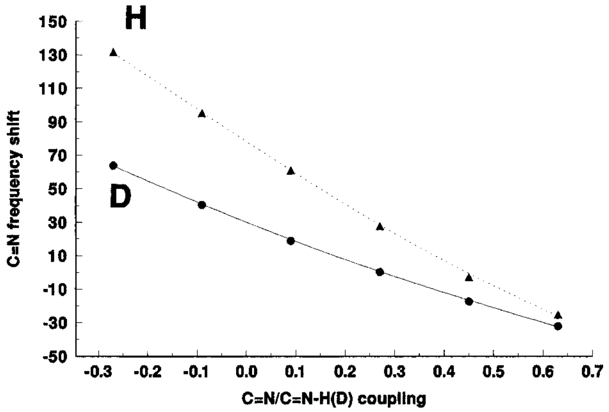

Figure 2. Shift in the C=N stretching frequency ($\nu_{C=N(H)} - \nu_{C=N}$, and $\nu_{C=N(D)} - \nu_{C=N}$) due to protonation of $H_2C{=}(CHCH{=})_3NH$ as a function of C=N/C=NH coupling force constant. The bending force constant is kept constant at 1.08 mdyn/Å. The triangle is for C=NH and the circle for C=ND.

$H_2C{=}(CHCH{=})_3NH$ have similar $^{12}C/^{13}C{=}N$ isotope shifts, 31, 35, and 34 cm^{-1}, respectively, and similar $C{=}^{14}N/^{15}N$ isotope shifts, 14, 20, and 18 cm^{-1}, respectively. However, for the protonated imines, the corresponding deuterium isotope shifts at the nitrogen are significantly different, 53, 20, and 26 cm^{-1}. For protonated methylimine, the deuterium shift on nitrogen is much larger than the deuterium shift at the carbon, 53 and 17 cm^{-1}, respectively. For protonated *trans*-$CH_3CH{=}NCH_3$, the corresponding deuterium shifts are much closer, 20 and 14 cm^{-1}, and similarly for $H_2C{=}(CHCH{=})_3NH$, 26 vs 16 cm^{-1}, for nitrogen and carbon, respectively. Overall, the frequency shifts for simple imines, either due to protonation or isotopic substitution, can be very different from those for more complex imines.

4. C=N Frequency Shifts upon Protonation. In protonated $H_2C{=}(CHCH{=})_3NH$, although the C=N force constant is lower by 0.47 mdyn/Å compared with the unprotonated case, the C=N stretching frequency is higher by 22 cm^{-1}. This increase is obviously not due to the C=N stretching alone but is a result of coupling between the C=N stretching and the C=NH bending vibrational modes. To understand the factors that influence the C=N stretching frequency upon protonation, the change in the C=N stretching frequency is examined as a function of hypothetical C=NH bending force constants and C=N/C=NH coupling constants. The change in the C=N stretching frequencies due to protonation as a function of changing the C=N(H/D) bending force constant is shown in Figure 1. The change in the C=N stretching frequencies due to protonation as a function of changing the C=N/C=N(H/D) coupling force constant is shown in Figure 2. A slight increase in the C=NH bending force constant results in a larger increase in the C=N(H) stretching frequency upon protonation. For the deuterated case, the increase in the C=N(D) frequency is less sensitive to the C=NH bending force constant. Therefore, the difference in frequency shift between undeuterated and deuterated imines can be used as an indication of the size of the bending force constant. When the C=NH bending force constant is less than ~1.0 mdyn/rad^2, protonation leads to a decrease in the C=N(H) stretching frequency, whereas when the C=NH bending force constant is larger than ~1.0 mdyn/rad^2, protonation leads to an increase in the C=N(H) stretching frequency (*cf.* Figure 1).

The plot of the change in C=N stretching frequency against the C=N/C=NH coupling force constant has a large negative slope (*cf.* Figure 2), indicating that a slight increase in the C=N/C=NH coupling force constant results in a large decrease in C=N frequency upon protonation, for both the undeuterated and the deuterium case. From Figure 2, a negative C=N/C=NH coupling force constant will clearly increase the C=N(H/D) stretching frequency upon protonation. When the C=N/C=NH coupling force constant is smaller than 0.45 mdyn/rad, protonation leads to an increase in the C=N(H/D) stretching frequency. In this case, the larger the C=N frequency shift (upon protonation) between the undeteurated and deuterated cases, the smaller or more negative the coupling force constant (*cf.* Figure 2). Our GVB(6/12)/6-31G* results clearly show that the $C{=}NH^+$ stretching frequency and the deuterium isotope shift in protonated imines are significantly influenced by the C=NH bending and the C=N/C=NH coupling force constants. Overall, the larger the observed C=N frequency upon protonation or the deuterium isotope shift (C=N(D)), the larger the C=NH bending force constant or the smaller the C=N/C=NH coupling force constant.

The increase in the C=N(H) stretching frequency upon protonation is neither due to a negative C=N/C=NH coupling force constant, as suggested by the previous empirical calculations,[8] nor due to the large $C{=}NH^+$ stretching force constant as previously suggested.[3] The increase is mainly due to the strong contribution from the large C=NH bending force constant (1.08 mdyn/rad^2) and a positive coupling constant (0.30 mdyn/rad). The C=NH bending contribution also affects the magnitude of the $C{=}N(H/D)^+$ stretching frequency deuterium isotope shift. Consequently, the larger observed C=N stretching frequency upon protonation is due to a large C=NH bending force constant or a smaller C=N/C=NH coupling constant in polyimines. Due to the contributions of these two modes, the C=N stretching frequency is particularly sensitive to the bonding environment of the nitrogen.

Since the C=N stretching frequency and its deuterium isotope shift depend on the C=NH bending and the C=N/C=NH coupling force constants, the $C{=}N(H/D)^+$ stretching frequency deuterium isotope shift can be used as a measure of whether or not the nitrogen is protonated. It is generally proposed that a large C=N(H/D) stretching frequency deuterium isotope shift, ~25 cm^{-1} in rhodopsin and bacteriorhodopsin is characteristic of protonation.[5] The large deuterium shift can only be obtained when the proton is covalently bonded to the nitrogen, resulting in a large C=NH bending force constant that is responsible for shifting the C=N stretching frequency of protonated imines. Our calculations predict a deuterium isotope shift of 26 cm^{-1} for $H_2C{=}(CHCH{=})_3NH$, suggesting the nitrogen is indeed protonated. However, as pointed out previously,[2] there is no clear quantitative relationship between the deuterium isotope

TABLE 5: Calculated Rotational Barriers (kcal mol^{-1}) for Unprotonated and Protonated $H_2C{=}NH$ and *trans*-$CH_3CH{=}NCH_3$

imine	C=N	$C{=}NH^+$
$H_2C{=}NH$	70.3 (72.8[a])	83.8
$CH_3CH{=}NCH_3$	69.2	81.8

[a]Schmidt et al. MCSCF/6-31G* results.[24]

shift and the strength of the hydrogen bond. If the proton is not tightly bonded to the nitrogen, the observed frequency shift is expected to be much lower. Counterion dependencies in the C=N spectral region of protonated imines have been observed using resonance Raman and Fourier transform infrared (FTIR) spectroscopy.[26] The counterion can affect the $C{=}NH^+$ environment. Since interaction of the proton with the counterion changes the C=NH bending force constant, this perturbation affects the $C{=}NH^+$ frequency more than the $C{=}ND^+$ frequency. The nonbonded counterion results in near-equal shifts of both frequencies. FTIR spectra[26] showed that the C=N stretching vibrational frequency of the protonated imine is sensitive to which halide (Cl^-, Br^-, I^-) is present as a counterion. The results show that the halide ions form salt bridges with the protonated imine. For *N*-retinylidene-*n*-butylammonium (NRBA) in $CHCl_3$, the C=N vibrational frequency is measured to be 1652 cm^{-1} for Cl^-, 1649 cm^{-1} for Br^-, and 1644 cm^{-1} for I^-.[26] The $C{=}NH^+$ stretching frequency correlates with the strength of the bond formed with the halide. The more strongly bonded halide would have a higher $C{=}NH^+$ frequency due to the expected increase in the C=NH bending force constant (*cf.* Figure 1).

5. C=N Rotational Barrier. Another important factor that can be used to determine the strength of the C=N bond is the barrier to rotation around the double bond. The twisted structures are considered to be the transition state for singlet rotation. The twisted diradical structures for the unprotonated and protonated methylimines were obtained at the GVB(6/12)/6-31G* level of calculation.[19] The C−N bond in the twisted structures is about 1.45 Å, which is very close to the MCSCF/3-21G* geometry[24] of 1.46 Å, showing a typical C−N single bond. The $C{-}NH_2^+$ bond in the twisted structure is slightly longer. In the twisted structure of protonated *trans*-$CH_3CH{=}NCH_3$, the single C−N bond becomes longer by 0.015 Å upon protonation.

The GVB(6/12)/6-31G* results of the rotational barrier for methylimine and *trans*-$CH_3CH{=}NCH_3$ are given in Table 5. For methylimine, the barrier is 70.3 kcal mol^{-1}, in agreement with the MCSCF/6-31G* result of 72.8 kcal mol^{-1}.[22] Upon protonation, the barrier is increased by 13 kcal mol^{-1}, indicating an increase in the C=N bond strength. From methylimine to *trans*-$CH_3CH{=}NCH_3$, the rotational barrier decreases by 1 kcal mol^{-1}, while it decreases by 2 kcal mol^{-1} for the protonated species. The results show that the C=N bond strength will decrease with an increase in conjugation.

6. Electronic Structures. Figure 3 illustrates the GVB(6/12)/6-31G* results of Mulliken charge distribution for unprotonated and protonated $H_2C{=}(CHCH{=})_6NH$. The net atomic charges on carbon are almost constant in the unprotonated species, due to conjugation.[22] Upon protonation, the positive charge on NH_2^+ causes a strong charge alternation along the chain, as illustrated in Figure 3. An increase of the C=NH bending force constant, and thus the $C{=}NH^+$ frequency, can be viewed as due to the increased negative charge on nitrogen and increase in positive charge on the adjacent carbon. The result is a stronger NH^+ interaction[25, 8] and a larger electrostatic repulsion between the hydrogen and the carbon.

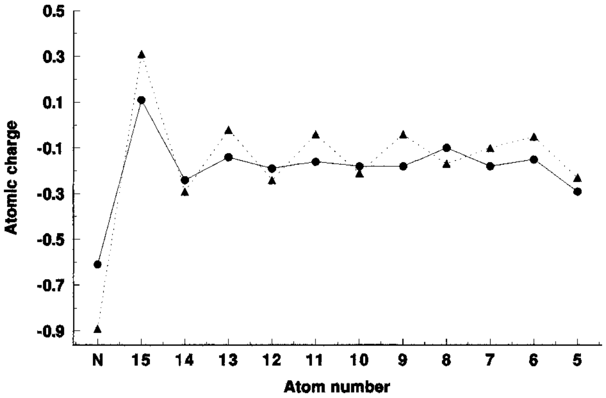

Figure 3. Mulliken charge distribution for unprotonated (solid line) and protonated (dashed line) $H_2C{=}(CHCH{=})_6NH$. The atom numbering is the same as in ref 22.

IV. Conclusions

In summarizing our results, the following conclusions can be drawn.

1. The GVB(6/12)/6-31G* geometries of methylimine are much improved over the previous ab initio (HF and GVB) calculations. The calculated GVB(6/12)/6-31G* frequencies for methylimine are in good agreement with the available experimental data.
2. Generally, the C=N bond is longer by 0.02 Å for protonated imines compared to unprotonated imines. The GVB(6/12)/6-31G* C=N stretching force constants show a decrease (by 0.47 mdyn/Å for polyimines) upon protonation. However, a higher C=N(H) stretching frequency has been obtained, along with a large deuterium isotope shift, mainly due to a strong contribution from the large C=NH bending force constant.
3. The C=N(H) stretching frequency deuterium isotope shift is a measure of whether the imine nitrogen is protonated and the strength of the counterion interaction to the protonated imine.
4. Protonation increases the C=N π bond energy and changes the electronic environment around the C=N bond.

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