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Supplementary Material Available: In-plane vibrational frequencies and corresponding potential energy distribution for methylimine and for a hypothetical methylenimmonium ion (8 pages). Ordering information is given in any current masthead page.

Rehybridization of the C=N Bond upon Protonation of Methylimine Increases the C=N Stretching Force Constant

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Abstract: Ab initio calculations have been carried out at the generalized valence bond and self-consistent field levels for methylimine and protonated methylimine. The GVB calculations show that the C=N stretching force constant increases upon protonation by ~0.51 mdyn/Å. The increase in the C=N stretching force constant translates into an increase in the C=N stretching frequency of ~30 cm^{-1}. This suggests that comparable frequency shifts, which are observed when other Schiff's bases are protonated, are also due primarily to the increase in the C=N stretching force constant.

Nitrogen and carbon are able to change their hybridization readily to form different kinds of bonds. It is not surprising, therefore, that their interrelationship plays important roles in biological systems. One of these nitrogen-carbon bonds, the Schiff's base (C=N) linkage, has attracted interest because of its occurrence in the rhodopsin visual pigment,[1] in bacteriorhodopsin and its photocycle derivatives,[2] and in pyridoxal-based enzyme systems.[3] Metallopophyrin and metallochlorin Schiff's bases have been synthesized recently and the possibility that these occur in vivo has been raised.[4]

The fact that Schiff's base linkages are versatile in their physical and chemical properties no doubt accounts for their importance in biological catalysis. The C=N bond, for example, is fairly labile and can be hydrolyzed and re-formed readily. Protonation of the C=N nitrogen in a Schiff's base containing chromophore generally leads to a marked red shift in the chromophore absorption spectrum. This reaction is of importance in controlling the optical properties of the retinal Schiff's base in the visual pigment rhodopsin.

An interesting aspect of the Schiff's base protonation reaction (and reactions with Lewis acids in general)[5] is the observation that the C=N stretching frequency increases. The molecular mechanism underlying this increase is not well-understood. In the preceding paper, we point out the analogy that can be made between the vibrational properties of Schiff's bases and those of nitriles. In nitriles, the observed decrease in the C≡N bond length and the accompanying increase in the C≡N vibrational frequency upon reaction with a Lewis acid have been interpreted in terms of an increase in the force constant of the C≡N bond.[6] This interpretation suggests that a similar effect could be responsible for the increase in the C=N stretching frequency in Schiff's bases upon reaction with Lewis acids.

Methylimine, the simplest Schiff's base, and its protonated derivative provide model systems which can be used to study the electronic changes in the C=N bond when the nitrogen lone pair is encumbered. These species are difficult to deal with experimentally, however, and only a few reports of their vibrational properties have appeared. Milligan,[7] in infrared spectroscopic studies of the photolysis of methyl azide, assigned the frequency of the C=N stretching mode of methylimine at 1628 cm^{-1}. Confirmation of methylimine as a photolysis product was obtained by Moore et al.[8] in a study of diazomethane which showed that the C=N stretching vibration was observed at 1642 cm^{-1}. The difference in frequency between this result and that reported in

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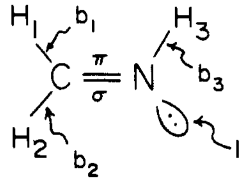
Milligan's earlier work[7] may have been due to the presence of hydrogen cyanide which occurred as a second product in the matrix prepared by Moore et al.[8] Curiously, substitution of the hydrogens in methylimine by fluoride, i.e., perfluoromethanimine,[9] increases the C═N vibrational mode to 1740 cm^{-1} despite the increase in mass of the substituents.

Theoretical work on vibrational frequencies in the methylimine system has also been done. Beginning with the results of Moore et al.,[8] Botschwina[10] used ab initio methods and a small basis set to calculate the force field of methylimine. For methylenimmonium ion (protonated methylimine) calculations of neither the C═N stretching force constant nor of the contribution of the s and p orbitals to the sp^2 hybrid forming the C═N bond have appeared. However, Eades et al.,[11] using SCF calculations and a PRDDO optimized geometry, estimated that the C═N—H bond angle increases by approximately 10° and that the C═N bond length increases by 0.019 Å upon protonation. In the same work, the vibrational frequencies for methylimine and for methylenimmonium ion were calculated, but for neither molecule were attempts made to assign the frequencies or estimate the force constants of the C═N stretching mode. Kollman and co-workers,[12] in SCF calculations of the electronic structure of $CH_2NH_2^+$, indicated that the nitrogen appears to be partially negatively charged.

With this previous work in mind we have carried out ab initio electronic structure calculations for methylimine and methylenimmonium ion, at the generalized valence bond (GVB)[13] and self-consistent field (SCF) levels. The GVB results show an increase in the nitrogen s character contributing to the C═N σ bond, an increase of 0.51 mdyn/Å in the C═N force constant, a slight decrease in the C═N bond length, and a decrease in the carbon electronic charge when methylimine is protonated.

Theoretical Details

In the GVB calculations the 12 valence electron of methylimine were represented by 6 electron pairs, each of which was represented by two natural orbitals. The assignment of the electron pairs to the molecular structure is given as:



where b_1, b_2, b_3, and l represent the CH's, the NH, and the nitrogen lone pair, respectively, and the σ and π correspond to the particular bonds between nitrogen and carbon. For the protonated methylimine a NH bond (b_4) replaces the lone pair l.

The expansion basis was the Huzinaga[14] 9s5p set on both carbon and nitrogen and the Dunning[15] 4s set on each hydrogen. These were augmented with polarization functions (d's for carbon and nitrogen ($\alpha = 0.75$ and 0.80, respectively) and p's for each hydrogen ($\alpha = 1.0$)]; the resulting basis was (9s5p1d/4s1p) and was contracted to [3s2p1d/2s1p] by using the general contraction of Raffenetti.[16] Total charge distribution as well as the percent s and p character in the nitrogen contribution to the C═N bond were calculated from the natural orbitals of the GVB wave function by using the Mulliken population analysis.[17]

To calculate the C═N stretching force constant we used the following geometry optimization procedure. As a starting point, we fixed all geometric parameters for both methylimine and methylenimmonium ion at the Eades et al.[11] PRDDO optimized geomerty and varied the C═N distance by 0.025 au (0.01323 Å) symmetrically about the initial minimum energy geometry. This calculation gives the energy at a given C═N distance and the new equilibrium geometry. For both molecules the resulting potential energy curves were fit to a fourth order polynomial[18] in $(R - R_{eq})$ where R_{eq} is the calculated C═N bond length, and the force constant for the C═N stretching mode was determined from the coefficient of the quadratic term in this expansion. All calculations were carried out by using the Argonne National Laboratory Collection of Electronic Structure Codes (QUEST-164). In particular, the integrals were done by using the program ARGOS written by Pitzer,[19] and the GVB calculations were done by using the program GVB-164 written by Bair.[20] The calculations were done on an FPS 164 attached array processor.

Table I. Methylimine Potential Curve:[a,b] Total Energy for the C═N Stretching Motion

$r_{(C═N)}$	E_{SCF} (+94.0 au)	E_{GVB} (+94.0 au)
1.222	−0.050 33	−0.148 01
1.236	−0.051 55	−0.150 31
1.249	−0.052 16	−0.152 01
1.262	−0.052 18[c]	−0.153 15
1.275	−0.051 68	−0.153 79
1.289	−0.050 64	−0.153 95[c]
1.302	−0.049 24	−0.153 67
1.315	−0.047 29	−0.152 95
1.328	−0.045 12	−0.151 96
1.341	−0.042 50	−0.150 58

[a] Energy in hartrees and bond length in Å. [b] Points closest to the equilibrium geometry used for a quadratic polynomial fit. [c] Computed point nearest the equilibrium geometry.

Table II. Methylenimmonium Ion Potential Curve:[a,b] Total Energy for the C═N$^+$ Stretching Motion

$r_{(C═N^+)}$	E_{SCF} (+94.0 au)	E_{GVB} (+94.0 au)
1.242	−0.406 378	−0.506 805
1.255	−0.407 058	−0.508 163
1.268	−0.407 179[c]	−0.508 968
1.282	−0.406 776	−0.509 238[c]
1.295	−0.405 888	−0.509 043
1.308	−0.404 572	−0.508 417
1.321	−0.402 836	−0.507 373

[a,b] See corresponding footnotes in Table I. [c] Computed point nearest the equilibrium geometry.

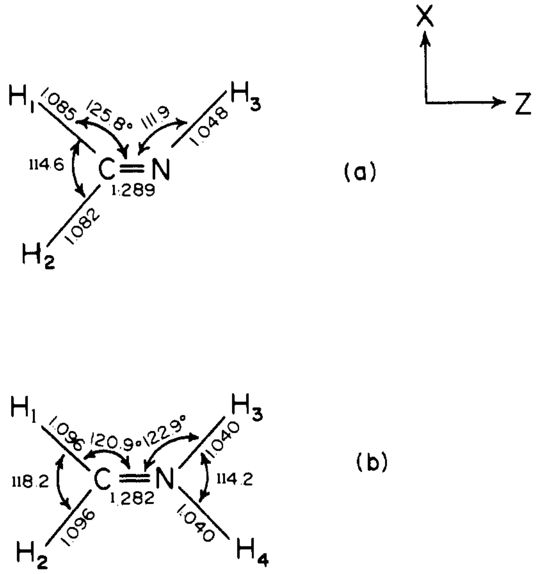


Figure 1. Geometry of methylimine (a) and protonated methylimine (methylenimmonium ion) (b): bond lengths in angstroms and bond angles in degrees (also see text for details).

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Table III. Calculated[a] Force Constants[b] for the C═N[c] and C═N^{+}[d] Stretching Motions

force constant	C═N	C═N^{+}
k_{GVB}	11.14	11.65
k_{SCF}	13.77	13.25

[a] From a polynomial fit of the GVB and SCF potential curves (see text for details). [b] Quadratic valence force constant in mdyn/Å. [c] Methylimine [d] Methylenimmonium ion.

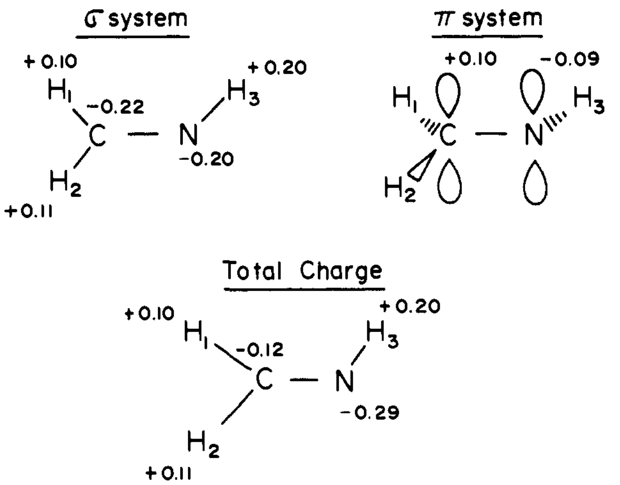

Figure 2. σ system, π system, and total charge distribution for methylimine.

Results

Calculated potential curves at the GVB and SCF level for the C═N and C═N^{+} stretching modes are shown in Tables I and II, respectively. Figure 1 shows the calculated GVB equilibrium geometry for methylimine and the protonated derivative. The protonated species shows a potential minimum at an energy lower than the unprotonated one. This is in agreement with previous calculations in which a small basis set and the SCF formalism were used.[11,12] The GVB calculation predicts that upon protonation of methylimine, the C═N bond will be slightly shorter than in the unprotonated species (1.282 and 1.289 Å, respectively). On the other hand, our SCF calculation predicts, in agreement with the SCF calculation of Eades et al.,[11] that the bond distances of the protonated derivative (1.268 Å) will be slightly longer than the neutral species (1.262 Å).

The fitted potential surfaces were used to determine the coefficients of the quadratic terms which in turn give the force constants for the C═N and C═N^{+} stretching modes. These are shown in Table III. We estimated the anharmonicity corrections and found them to be negligible. The protonated species at the GVB level shows an increase in the C═N^{+} stretching force constant, relative to the C═N stretching force constant, of 0.51 mdyn/Å, while at the SCF level this force constant shows a decrease of 0.52 mdyn/Å; in addition, the values of both the unprotonated and protonated force constants at the SCF level are higher than at the GVB level. It is generally recognized that SCF calculations overestimate force constants by between 10 and 30%.[21] Since the GVB wave function contains a more appropriate mixture of ionic and covalent terms and separates to the correct asymptotic products, the GVB force constants should be more reliable.[13]

One may think of the GVB wave function as being the SCF function plus various correction terms.

$$|\mathrm{GVB}\rangle = |\mathrm{SCF}\rangle + |\text{correction terms}\rangle$$

The "correction terms" correct for the wrong distance-dependent behavior of the |SCF⟩, i.e., when bond lengths are changed. We are not too concerned with the |SCF⟩ predicted trend upon protonation since we realize it is a much less complete function than the GVB. When one has two approximate wave functions and one is considerably less approximate than the other, it seems prudent to trust the predictions of the more complete functions over those of the less complete functions. Note also that the GVB is equivalent to an SCF with limited configuration interactions. The GVB contains electron correlation corrections while the SCF

Table IV. Methylimine: Electron Distribution

	orbitals						
atom	s_{σ}	p_{σ}	d_{σ}	p_{π}	d_{π}	σ	π
carbon	3.19	1.98	0.05	0.89	0.01	5.22	0.90
nitrogen	3.58	2.60	0.02	1.08	0.01	6.20	1.09
H_1	0.89	0.01		0.00		0.90	0.00
H_2	0.88	0.01		0.00		0.89	0.00
H_3	0.78	0.02		0.00		0.80	0.00
Total						14.01	1.99

Table V. Methylenimmonium Ion: Electron Distribution

	orbitals						
atom	s_{σ}	p_{σ}	d_{σ}	p_{π}	d_{π}	σ	π
carbon	3.23	2.03	0.04	0.61	0.02	5.30	0.63
nitrogen	3.42	2.41	0.03	1.35	0.01	5.86	1.36
H_1	0.77	0.01		0.00		0.78	0.00
H_2	0.77	0.01		0.00		0.78	0.00
H_3	0.61	0.02		0.00		0.63	0.00
H_4	0.61	0.02		0.00		0.63	0.00
Total						13.98	1.99

Table VI. Electron Distribution of the σ Bond System[a]

bond[b]	atom	orbital[c]/atom[d]	methylimine	methylenimmonium ion
H_1–C	carbon	s/C	0.32	0.33
		p/C	0.57	0.61
		s/H_1	0.14	0.07
	hydrogen(1)	s/H_1	0.81	0.75
		s/C	0.09	0.12
		p/C	0.11	0.12
H_2–C	carbon	s/C	0.31	0.33
		p/C	0.58	0.61
		s/H_2	0.13	0.07
	hydrogen(2)	s/H_2	0.80	0.75
		s/C	0.09	0.12
		p/C	0.12	0.12
C–N	carbon	s/C	0.33	0.29
		p/C	0.51	0.49
	nitrogen	s/N	0.31	0.42
		p/N	0.58	0.52
N–H_3	nitrogen	s/N	0.20	0.33
		p/N	0.69	0.62
		s/H_3	0.11	0.07
	hydrogen(3)	s/H_3	0.75	0.61
		s/N	0.04	0.13
		p/N	0.23	0.27
N–(lone pair)	nitrogen	s/N	0.41	
		p/N	0.51	
	lone pair	s/N	0.57	
		p/N	0.50	
N–H_4	nitrogen	s/N		0.33
		p/N		0.62
		s/H_4		0.07
	hydrogen(4)	s/H_4		0.61
		s/N		0.13
		p/N		0.27

[a] Calculated from Mulliken population analysis. [b] See Figure 1 for the particular geometry. [c] s and p stands for s and p orbitals, respectively. [d] C, N, and H stands for the carbon, nitrogen, and hydrogen atoms involved in the particular bond.

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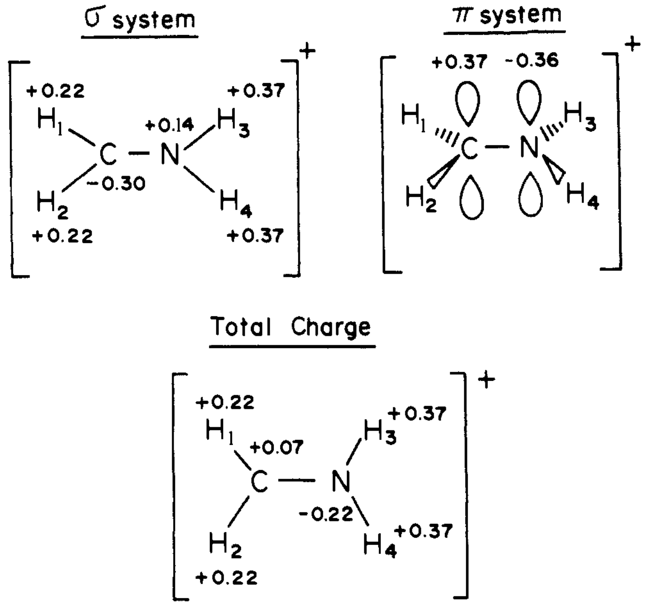

Figure 3. σ system, π system, and total charge distribution for methylenimmonium ion.

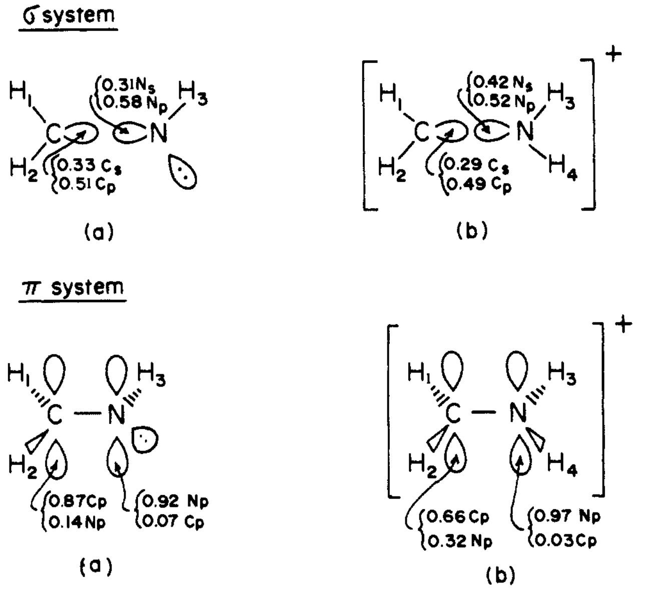

Figure 4. s-p and p electron distribution of the σ and π systems in the C=N bond of methylimine and methylenimmonium ion.

does not.

Tables IV and V present the Mulliken population analysis for both the protonated and unprotonated methylimine species calculated at the minimum energy geometry. Figures 2 and 3 show the corresponding contribution of the σ and π systems to the total electron distribution, while the sp electron distribution to various bonds in the σ system is shown in Table VI. Figure 4 indicates the change in the sp character of the nitrogen when methylimine is protonated. Under the same circumstances, Figure 4 also shows the electron distribution in the π systems in the C=N and C=N$^+$ bonds.

Discussion

Further insight into the mechanism responsible for the increase in the C=N stretching force constant upon protonation may be gleaned from the detailed electron distribution predicted by the GVB functions used in this work. If the nitrogen atom in methylimine did not use its 2s electrons in the bonding to the H or CH_2 group, we would expect a CNH angle of 90° and no nitrogen 2s character in either the C-N or N-H σ bonds. The calculated value of 111.9° for the CNH angle in CH_2NH reflects the extent to which the nitrogen 2s electrons participate in the bonding, and from Figure 4 we see that the GVB calculations allot 0.31 electron from the nitrogen 2s to this C-N bond. When methylimine is protonated at the nitrogen lone pair, the CNH angle increases further to 122.9° and the calculated number of nitrogen 2s electrons in the C-N bond increases to 0.42. This enhanced nitrogen 2s character in the C-N bond is reflected in a smaller bond length in the positively charged ion relative to the neutral species and in the increase in the stretching force constant.

The calculations above indicate that it is possible to attribute the increase in the C=N stretching force constant in methylenimmonium species to a change in the electronic environment of the C=N bond upon protonation of methylimine. This increase in the C=N stretching force constant for the protonated species translates into an increase in the C=N stretching frequency of ~30 cm^{-1} (see preceding paper[5]) and suggests that the same kind of mechanism may be responsible for the observable increase in the C=N stretching frequency in protonated or Lewis acid-complexed Schiff's bases.

Several studies have suggested that when one protonates a polyene Schiff's base the π bond order decreases resulting in a corresponding decrease in the C=N force constant.[1b,c] If the encumbered lone pair mechanism (rehybridization model) is to be dominant for such systems, then the change in the π bond order and π component of the C=N force constant must be smaller than these earlier studies predict. We are extending our ab initio model to conjugated systems in order to test this hypothesis. Note, however, that numerical experiments within the normal coordinate model suggest[5] that the increase in the C=N stretching frequency observed upon protonation in a variety of molecules cannot be reproduced with a "sensible" set of interaction force constants when there is a decrease of 0.3 mdyn/Å in the C=N force constant.[5]

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Registry No. Methylimine, 2053-29-4; protonated methylimine, 28963-72-6.