values approximately 0.5 and 1 MHz, respectively, lower than expected. This implies, we believe, that the large majority of these sites are coordinated to nonframework cations. Certainly, in Na–A zeolite (Si/Al = 1), we expect that the vast majority of the linkages will exhibit coordination to sodium.

Pauling's rules predict that the nonframework cations should preferentially coordinate to the Al–O–Si and Ga–O–Si linkages over the Si–O–Si linkage.[19] The nearly identical e^2qQ/h, η, and δ_i observed for the Si–O–Al linkage in Na–A and Na–Y suggest that the local electronic environment of this oxygen is quite similar in both cases, and, within our resolution, coordinated to nonframework cations. Although we have not yet detected uncoordinated Al–O–Si and Ga–O–Si linkages, we expect their e^2qQ/h values to be larger than those of coordinated species. The results for the Si–O–Si linkage in Na–Y are more ambiguous. The static e^2qQ/h is similar to the framework Si–O–Si linkage in low cristobalite, but the MASS value is intermediate to that expected for nonframework cation coordinate and the strictly bicoordinate species. As an independent check, therefore, we have made the barium-exchanged species. Large group 2 nonframework cations tend to shift the oxygen resonances to more deshielded values.[21] We observe a change in the chemical shift of both the Si–O–Si

and Si–O–Al linkages (still, Al–O–Si has a more deshielded chemical shift), thereby suggesting that both linkages may be coordinated, at least in the barium variant of Y zeolite.

In the gallosilicates, the e^2qQ/h values for Si–O–Si linkage for all of the species are similar to that found in low cristobalite, in both the MASS and static cases. This would tend to indicate that the nonframework cations are preferentially coordinated to the Si–O–Ga linkage at the expense of the Si–O–Si linkage.

Finally, presented in Table III is a comparison between the experimentally observed average ^{17}O e^2qQ/h values for Si[^{17}O]Si, Si[^{17}O]Al, Si[^{17}O]Ga, and Al[^{17}O]P, and those prediced by the Townes–Dailey analysis presented in this publication, and from the wholly empirical correlation presented previously.[6] Although more systems should clearly be studied to firmly establish such trends, we believe that the results of Table III strongly suggest, for purely bicoordinate oxygen linkage (Si–O–Si, Al–O–P), that the T–D analysis is more reliable, while in systems having additional nonframework cation coordination, that use of the empirical correlation is most appropriate.

(21) Turner, G. L.; Chung, S. E.; Oldfield, E. *J. Magn. Reson.* **1985**, *64*, 316.

Factors Influencing the C=N Stretching Frequency in Neutral and Protonated Schiff's Bases

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Abstract: The C=N stretching frequency has been studied in a series of aromatic Schiff's bases, their protonated derivatives, and their reaction products with other Lewis acids. Protonation, deuteration, or reaction with BF_3 increases the C=N stretching frequency in a range from 1 to 80 cm^{-1}. Linear polyene Schiff's bases show similar behavior: an increase in the C=N frequency of ~30 cm^{-1} is observed upon complexation of *trans*-retinal Schiff's base by BF_3. The magnitude of the increase in the C=N vibrational mode is dependent on the extent of conjugation in the aromatic system, on the nature of the substituent, and on the strength of the Lewis acid. In the NMR spectra of the protonated or complexed species a downfield chemical shift of the protons nearby the C=N bond is observed which suggests that the nitrogen electronegativity increases in the reaction product relative to the free Schiff's base. These observations, plus the similarities in behavior of Schiff's bases and nitriles, suggest that rehybridization at the Schiff's base nitrogen occurs on reaction of its lone pair with Lewis acids to increase the C=N bond order. Ab initio calculations on the Schiff's base, methylimine (see following paper), support this idea as the C=N bond length decreases and the C=N stretching force constant increases by 0.51 mdyn/Å upon protonation. Normal coordinate analysis of this species, of the model structure, $CH_3HC=NCH_3$, and of their protonated and deuterated derivatives are reported here which show that an increase in the stretching force constant of this magnitude leads to an increase of ~30 cm^{-1} in the frequency of the C=N stretching vibration. Analogous normal coordinate calculations were also carried out for the BF_3 addition product which show that a similar increase in C=N stretching force constant upon complexation is likely. The results indicate that rehybridization effects, in particular, an increase in the s orbital contribution from the protonated nitrogen to the sp^2 hybrid orbital in the Schiff's base linkage, are primarily responsible for the increase in the C=N stretching frequency upon complexation of a Schiff's base by a Lewis acid.

Schiff's base (**1**) and protonated Schiff's base (**2**) C=N vibrational[2] modes have been studied for at least the past three decades.[1] Part of the interest in these species derives from the
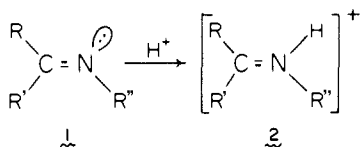
observation of functionally significant Schiff's base linkages in biological systems, for example, in pyridoxal enzymes[2] and, more recently, in rhodopsin, bacteriorhodopsin, and related visual cycle intermediates and models.[3] In rhodopsin, the retinal chromophore

(1) (a) Fabian, M. J.; Legrand, M.; Poirier, P. *Bull. Soc. Chim. Fr.* **1956**, 1499–1509. (b) Fabian, M. J.; Legrand, M. *Ibid.* **1956**, 1641–1643.

(2) (a) Witkop, B.; Beiler, T. W. *J. Am. Chem. Soc.* **1954**, *76*, 5589–5597. (b) Karube, Y.; Ono, Y.; Matsushima, Y.; Ueda, Y. *Chem. Pharm. Bull.* **1978**, *26*, 2642–2648. (c) Ledbetter, J. W. *J. Phys. Chem.* **1982**, *86*, 2449–2451. (d) Benecky, M. J.; Copeland, R. A.; Hayes, T. R.; Lobenstine, E. W.; Rava, R. P.; Pascal, R. A., Jr.; Spiro, T. G. *J. Biol. Chem.* **1985**, *260*, 11663–11670. (e) Benecky, M. J.; Copeland, R. A.; Rava, R. P.; Feldhaus, R.; Scott, R. D.; Metzler, C. M.; Metzler, D. E.; Spiro, G. T. *Ibid.* **1985**, *260*, 11671–11678.

is bound to the opsin protein moiety through a Schiff's base linkage, and resonance Raman spectroscopy has been used extensively to monitor changes in the C=N stretching frequency during the rhodopsin protocycle. The C=N stretching mode in the neutral species occurs at 1620 cm^{-1}. This increases to 1655 cm^{-1} upon protonation and to 1630 cm^{-1} upon deuteration. In bacteriorhodopsin, similar frequency changes, presumably originating in the protonated Schiff's base, occur at stages in the photocycle and suggest different degrees of protein–chromophore interaction for the various intermediates.[3j-k,m]

Recent work from this laboratory[4a,b] on Schiff's bases formed between formylated metalloporphyrins or metallochlorins and primary amines shows that upon protonation of these aromatic Schiff's bases there is an increase in the C=N stretching frequency as well. For example, for the Schiff's base of Ni(II) porphyrin *a* the C=N stretching vibration occurs at 1639, 1650, and 1640 cm^{-1}, respectively, for neutral, protonated, and deuterated species. Accompanying the protonation reaction, there is a marked optical red shift in the visible region,[4] as also occurs in the polyene case.[3a-c,i,m] The latter observation has led to the suggestion that the red shifts observed for chlorophyll in vivo may originate, at least in part, from similar phenomena, i.e., from formation and protonation of Schiff's base linkages in the protein environment.[4c,5]

While the origin of the optical red shift has been explored theoretically in both aromatic heterocycle[4b,5b] and polyene cases,[6] the mechanism underlying the increase in the characteristic Schiff's base frequency upon protonation remains obscure. Both the resonance structures (4, 5) and the increase in the reduced mass
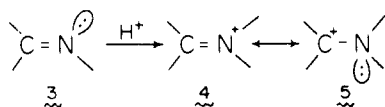
of the nitrogen suggest that the C=N$^+$ vibrational frequency should decrease. In the visual pigments and their model compounds, the increase in ν(C=N) upon protonation has been attributed to the interaction between the C=N stretching mode and the C=N—H bending mode.[3b,c,j-l] As pointed out by Marcus et al.,[31] however, the stretch/bend interaction model does not provide a ready explanation for the increase in the C=N vibrational mode which occurs when retinal Schiff's base derivatives are methylated.

Increases in the unsaturated carbon–nitrogen stretching vibrational frequency upon reaction with a Lewis acid have been reported for other systems. For example, IR studies on ketimines (RR'C=NR″) indicate that the increase in ν(C=N) which is observed when the nitrogen lone pair is shared with a Lewis acid substituent (e.g., H$^+$ or BF$_3$) results from an increase in the C=N bond order.[7] Similarly, when nitriles (6) react with Lewis acids,
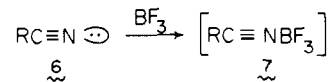
such as BF$_3$ (7) and BCl$_3$, the C≡N stretching mode increases in frequency. This behavior has also been attributed to an increase in the C≡N stretching force constant and to a decrease in the C≡N bond distance.[8] Because of the structural analogies between these species and the Schiff's base system, these results suggest that a similar mechanism may occur for the Schiff's base C=N group.

In the work described here, we have explored these possibilities by carrying out nuclear magnetic resonance and Raman spectroscopic studies on aromatic Schiff's bases and protonated, deuterated, and BF$_3$ derivatives. These systems serve as simple models for the aromatic metalloporphyrin systems and also allow us to compare the behavior of the C=N group in aromatic and linear polyene Schiff's bases. In the aromatic models, both protonation and reaction with BF$_3$ increase the C=N stretching frequency, and NMR data show an increase in the electronegativity of the nitrogen. These results are similar to those described for the ketimine and nitrile systems and suggest that electron redistribution in the C=N system occurs upon reaction such that the C=N stretching force constant increases. Ab initio calculations on the Schiff's base methylimine and its protonated derivative show that an increase in C=N bond order occurs upon protonation, thereby supporting this rehybridization model (see following paper).[9a] Normal coordinate calculations have been carried out to assess the effect of the increased C=N stretching force constant on the C=N stretching frequency. We have also carried out vibrational analyses of models in which the C=N stretching force constant is allowed to decrease upon protonation in order to explore the predictions of the stretch/bend interaction model in light of a restricted set of force constants. The force constants selected are consistent with work on related molecules which has appeared in the literature recently. For both types of force fields, we systematically varied the force constants of the modes which influence $\nu_{C=N}$ in order to understand their various contributions to the observed behavior. The results of these analyses indicate that the electron density redistribution which occurs upon protonation plays a major role in determining the C=N stretching frequency; the stretch/bend interaction is prominent to a much lesser extent. Preliminary accounts of this work have appeared;[9b,d] we report in more detail elsewhere on the properties of linear polyene (retinal) Schiff's base–Lewis acid complexes.[9c]

Experimental Methods

Materials. Benzaldehyde, *trans*-retinal, methylamine, *n*-butylamine, *tert*-butylamine, benzophenone, bromobenzene, and benzonitrile were obtained from Aldrich Chemical Co. 2-Naphthaldehyde and 9-anthraldehyde were obtained from Alfa Products.

Imines. *N*-Benzylidene-*n*-butylamine, 2-naphthylidene-*n*-butylamine, and 9-anthrylidene-*n*-butylamine were prepared by reaction of the ap-

(3) (a) Ottolenghi, M. *Adv. Photochem.* **1980**, *12*, 97–200. (b) Aton, B.; Doukas, A. G.; Narva, D.; Callender, R. H.; Dinur, U.; Honig, B. *Biophys. J.* **1980**, *29*, 79–94. (c) Smith, S. O.; Pardoen, J. A.; Mulder, P. P. J.; Curry, B.; Lugtenburg, J.; Mathies, R. *Biochemistry* **1983**, *22*, 6141–6148. (d) Smith, S. O.; Myers, A. B.; Pardoen, J. A.; Winkel, C.; Mulder, P. P. J.; Lugtenburg, J.; Mathies, R. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 2055–2059. (e) Massig, G.; Stockburger, M.; Gärtner, W.; Oesterhelt, D.; Towner, P. *J. Raman Spectrosc.* **1982**, *12*, 287–294. (f) Aton, B.; Doukas, A. G.; Callender, R. H.; Becher, B.; Ebrey, T. C. *Biochemistry* **1977**, *16*, 2995–2999. (g) Rothschild, J. K.; Roepe, P.; Lugtenburg, J.; Pardoen, J. A. *Ibid.* **1984**, *23*, 6103–6109. (h) Lewis, A. *Phil. Trans. R. Soc. London, Ser. A* **1979**, *293*, 315–327. (i) Heyde, M. E.; Gill, D.; Kilponen, R. G.; Rimai, L. *J. Am. Chem. Soc.* **1971**, *93*, 6776–6780. (j) Smith, S. O.; Myers, A. B.; Mathies, R. A.; Pardoen, J. A.; Winkel, C.; van den Berg, E. M. M.; Lugtenburg, J. *Biophys. J.* **1985**, *47*, 653–664. (k) Kakitani, H.; Kakitani, T.; Rodman, H.; Honig, B.; Callender, R. *J. Phys. Chem.* **1983**, *87*, 3620–3628. (l) Marcus, M. A.; Lemley, A. T.; Lewis, A. *J. Raman Spectrosc.* **1979**, *8*, 22–25. (m) Bagley, K. A.; Balogh-Nair, V.; Croteau, A. A.; Dollinger, G.; Ebrey, T. G.; Eisenstein, L.; Hong, M. K.; Nakanishi, K.; Vittitow, J. *Biochemistry* **1985**, *24*, 6055–6071.

(4) (a) Ward, B.; Callahan, P. M.; Young, R.; Babcock, G. T.; Chang, C. K. *J. Am. Chem. Soc.* **1983**, *105*, 634–636. (b) Hanson, L. K.; Chang, C. K.; Ward, B.; Callahan, P. M.; Babcock, G. T.; Head, J. D. *Ibid.* **1984**, *106*, 3950–3958. (c) Ward, B.; Chang, C. K.; Young, R. *Ibid.* **1984**, *106*, 3943–3950.

(5) (a) Maggiora, L. L.; Maggiora, G. M. *Photochem. Photobiol.* **1984**, *39*, 847–849. (b) Petke, J. D.; Maggiora, G. M. *J. Am. Chem. Soc.* **1984**, *106*, 3129–3133.

(6) (a) Blatz, P. E.; Mohler, J. H. *Biochemistry* **1975**, *14*, 2304–2309. (b) Sheves, M.; Nakanishi, K. *J. Am. Chem. Soc.* **1983**, *105*, 4033–4039. (c) Baasov, T.; Sheves, M. *Ibid.* **1985**, *107*, 7524–7533. (d) Kakitani, H.; Kakitani, T.; Rodman, H.; Honig, B. *Photochem. Photobiol.* **1985**, *41*, 471–479. (e) Birge, R. R.; Hubbard, L. M. *J. Am. Chem. Soc.* **1980**, *102*, 2195–2205. (f) Freedman, K. A.; Becker, R. S. *Ibid.* **1986**, *108*, 1245–1251.

(7) Samuel, B.; Snaith, R.; Summerford, C.; Wade, K. *J. Chem. Soc. A* **1970**, 2019–2022.

(8) (a) Coerver, H. J.; Curran, C. *J. Am. Chem. Soc.* **1958**, *80*, 3522–3523. (b) Figeys, H. P.; Geerlings, P.; Berckmans, D.; Alsenoy, C. V. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 721–740. (c) Horac, M.; Vitek, A. *Interpretation and Processing of Vibrational Spectra*; Wiley: New York, 1978; pp 302–303. (d) Swanson, B.; Shriver, D. F.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 2182–2189. (e) Gerrard, W.; Lappert, M. F.; Pyszora, H.; Wallis, J. W. *J. Chem. Soc.* **1960**, 2182–2186.

(9) (a) López-Garriga, J. J.; Hanton, S.; Babcock, G. T.; Harrison, J. F., *J. Am. Chem. Soc.*, following paper in this issue. (b) López-Garriga, J. J.; Babcock, G. T.; Harrison, J. F. *Biophys. J.* **1985**, *47*, 96a. (c) López-Garriga, J. J.; Babcock, G. T.; Harrison, J. F. *J. Am. Chem. Soc.*, in press. (d) López-Garriga, J.; Babcock, G. T., Tenth International Conference on Raman Spectroscopy, Eugene, OR, 1986.

Table I. Diagonal and Off-Diagonal Force Constants[a] of Some Imines

compounds[b]	CN$_s$	CH$_s$	CC$_s$	NH$_s$	HCN$_b$	CNH$_b$	CCN$_b$	CN$_s$/CH$_s$	CN$_s$/NH$_s$	CN$_s$/CC$_s$	CN$_s$/HCN$_b$	CN$_s$/CNH$_b$	CN$_s$/CCN$_b$
allylimine	10.89	4.50	3.96	7.60	0.50	0.86	0.80	0.29	-0.05	0.56	0.31	0.58	0.25
methylimine[c]	11.14	4.92		5.73	1.05	0.88		0.26	0.09		0.48	0.68	
ethylidenimine	13.65	5.75	5.08	7.50	0.72	1.03	1.04	0.37	-0.09	0.34	0.35	0.59	0.15
propargylimine	13.60	6.01	6.17	7.60	0.70	1.01	1.00	0.28	0.02	0.68	-0.36	0.56	0.29
2-propanimine	13.40		5.10	7.40		1.06	0.70			0.60		0.59	
isocyanic acid	15.10					0.35						1.128	

[a] Units are mdyn/Å for the stretching (s) and stretching–stretching (s/s); mdyn/rad for the stretch–bending (s/b); mdyn Å/rad^2 for the bending (b) and bending–bending (b/b) force constants. [b] See ref 15a–d and 16a,b for detail of force fields. [c] See ref 9b.

Table II. F Matrix Elements[a] for the Model Structures[b]

C=N$_{(s)}$	N—H$_{(s)}$	C—C$_{(s)}$	C—H$_{(s)}$	N—C$_{(s)}$	CNH$_{(s)}$	CCN$_{(b)}$	HCN$_{(b)}$	CNC$_{(b)}$
(11.10) 10.60	(0.04)	0.58	0.15	0.58	(0.53)	0.42	0.28	0.42
	(5.40)	(0.16)	(-0.06)	(0.25)	(-0.15)	(-0.05)	(0.14)	(-0.04)
		4.30	0.23	-0.09	(0.09)	0.18	0.29	-0.08
			5.15	0.08	(0.09)	0.09	0.09	-0.15
				4.50	(0.09)	-0.05	-0.09	-0.06
					(0.85)	(0.15)	(0.20)	(0.11)
						0.70	0.09	-0.09
							0.62	-0.05
								0.70

[a] Force constants same units as Table I. [b] Table II contains the force field for two Schiff's base models; the unprotonated model is represented by the matrix elements without parentheses; the protonated force field contains the matrix elements in parentheses as well.

propriate aldehyde in a 4-h reflux with dry benzene containing an excess of *n*-butylamine.[4a,10] Following completion, excess *n*-butylamine and benzene were removed by vacuum evaporation. *N*-Benzylidene-*n*-butylamine was purified by vacuum distillation, while the 2-naphthylidene and 9-anthrylidene derivatives were recrystallized in a mixture of methylene chloride and petroleum ether. Retinylidene-*n*-butylamine was prepared as described.[3f]

Ketimines. α-Phenylbenzylidene-*n*-butylamine[11] was obtained as the reaction product between benzophenone and the amine with aluminum chloride as catalytic agent. α-Phenylbenzylideneamine was prepared by means of a Grignard reaction.[12]

Schiff's Base Derivatives. Protonated and deuterated derivatives were obtained by adding equivalent amounts of dry HCl(g) or DCl(g) to the corresponding imine solutions, by bubbling the acid through a solution of Schiff's base in ether until precipitation was completed, or by saturating the solvent with the acid and then adding equivalent amounts of the acidified solvent to the Schiff's base solution. The three methods gave identical results. The BF$_3$ derivatives were prepared by reacting a stoichiometric amount of ethyl ether–boron trifluoride complex with the particular imine in dimethyl sulfoxide (Me$_2$SO). All reactions were carried out after degassing solvents and imine solutions in a nitrogen environment. The solids were washed with ether, dried, and stored in a dry nitrogen atmosphere. The formation of the Schiff's bases from their parent aldehydes was, in general, indicated by a blue shift of the absorption spectra, while the formation of the Schiff's base complex was indicated, relative to the free base, by a red shift of the spectrum.[4,6,13]

Instrumental. Concentrations of the neutral and protonated Schiff's bases were typically 1.0–5.0 × 10^{-4} M in methylene chloride, chloroform, or dimethyl sulfoxide for optical measurements. Raman spectra of the aromatic Schiff's bases and their derivatives (~0.1–0.25 M in the different solvents) were obtained by using two different laser excitation frequencies: λ$_{ex}$ 647.1 nm for 2-naphthylidene and 9-anthrylidene derivatives and 514.5 nm for the other samples. Resonance Raman spectra of the retinal Schiff's base derivatives were recorded by using 441.6-nm excitation. A scan speed of 50 cm^{-1}/min, a time constant of 2.5 s, and a spectral resolution of 5 cm^{-1} were used in recording the Raman spectra on a Spex 1401 double monochromator. For the 250- and 60-MHz NMR spectra, aldehydes and imines were prepared in deuterated chloroform; protonated and deuterated derivatives were obtained by adding equivalent amounts of dry HCl or DCl gas.

Normal Coordinate Analysis. Vibrational analyses have been carried out for the Schiff's base CH$_3$CH=NCH$_3$ and for its protonated, deuterated, and BF$_3$-complexed derivatives. The Shimanouchi normal coordinate analysis program[14] was used for the calculations. The geometry

and force field of 2-propanimine,[15a] allylimine,[15b] ethylidenimine,[15c] propargylimine,[15d] and methylimine and methylenimmonium ion[9a,15f,16a] were employed to construct the geometry and force field for the normal mode calculation. Bond lengths (in angströms), as follows, were used: C–C = 1.46, C–H = 1.096, N–C = 1.45, N–B = 1.45, N–H = 1.04. The C=N bond lengths were taken from the ab initio calculations reported in the following paper:[9a] C=N (unprotonated) 1.289, and C=N (protonated and BF$_3$ complex) 1.281. The molecules were assumed to be planar with the following bond angles: CCN and HCN, 120.9°; CNC, 118.0° (unprotonated) and 122.9° (protonated); CNH and CNB, 122.9°. The CH$_3$ and the BF$_3$ groups were employed, as in other studies, as point masses.

Table I presents the main diagonal and off-diagonal force constants for a series of imines.[9a,15a–d,16a,b] A combination of these force fields with the force constants associated with the N–C motions in *N*-methylacetamide[15e] was used to construct an initial force field for the CH$_3$HC=NCH$_3$ Schiff's base and its protonated species. Semirefined force fields for the unprotonated and protonated models were obtained (see Table II) from a fit of the initial force field to the frequencies of the C=N stretch, C=N—H bend, and ring Schiff's base (PhHC=NR) motion in *N*-benzylidene-*n*-butylamine and its protonated and deuterated derivatives. For the C=N/C=N—H (stretch bend) interaction term a value of 0.53 mdyn/rad, which is similar to the interaction force constants reported in Table I and also to that calculated by Botschwina[16a] for methylimine, was used. Starting with these force fields for the various Schiff's base derivatives, we then determined the C=N stretching frequency as a function of the force constants of the principal modes which are likely to interact to produce the observed frequency in the neutral and complexed Schiff's bases. These calculations were carried out by fixing the force constants according to their vaues in Table II and allowing the force constant of interest to vary. We carried out these calculations for two different scenarios for the effect of complex formation on the C=N

(10) Santerre, G. M.; Hansrote, C. J., Jr.; Crowell, T. I. *J. Am. Chem. Soc.* **1958**, *80*, 1254–1257.

(11) Layer, R. W. *Chem. Rev.* **1963**, *63*, 489–510.

(12) Pickard, P. L.; Tolbert, T. L. *J. Org. Chem.* **1961**, *26*, 4886–4888.

(13) Honig, B.; Greenberg, A. D.; Dinur, U.; Ebrey, T. *Biochemistry* **1976**, *15*, 4593–4599.

(14) (a) Shimanouchi, T. *Computer Programs for Normal Coordinate Treatment of Polyatomic Molecules*; Tokyo University: Tokyo, Japan, 1969. (b) Nam, H.-H.; Leroi, G. E. *Spectrochim. Acta Part A* **1985**, *41*, 67–73.

(15) (a) Inamori, T.; Hamada, Y.; Tsuboi, M.; Koga, Y.; Kondo, S. *J. Mol. Spectrosc.* **1985**, *109*, 256–268. (b) Hamada, Y.; Tsuboi, M.; Matsuzawa, T.; Yamanouchi, K.; Kuchitsu, K. *Ibid.* **1984**, *105*, 453–464. (c) Hashiguchi, K.; Hamada, Y.; Tsuboi, M.; Koga, Y.; Kondo, S. *Ibid.* **1984**, *105*, 81–92. (d) Hamada, Y.; Tsuboi, M.; Takeo, H.; Matsumura, C. *Ibid.* **1984**, *106*, 175–185. (e) Sugawara, Y.; Hirakawa, A. Y.; Tsuboi, M. *Ibid.* **1984**, *108*, 206–214. (f) Eades, R. A.; Weil, D. A.; Ellenberger, M. R.; Farneth, W. E.; Dixon, D. A.; Douglass, C. H., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 5372–5377.
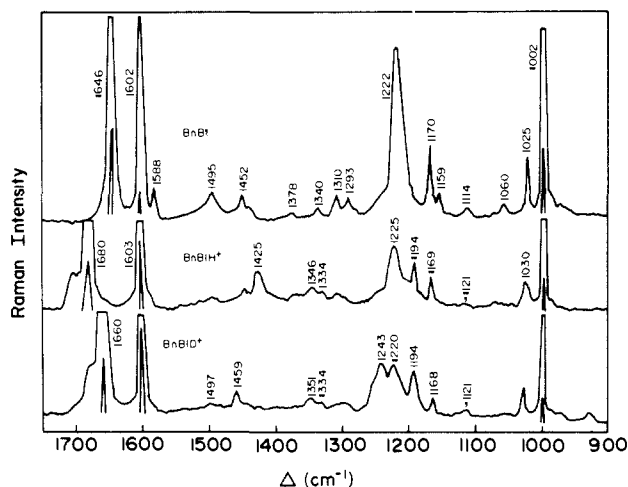
(16) (a) Botschwina, P. *Chem. Phys. Lett.* **1974**, *29*, 580–584. (b) Botschwina, P.; Nachbaur, E.; Rode, B. M. *Chem. Phys. Lett.* **1976**, *41*, 486–489. (c) Laswick, P. H.; Taylor, R. C. *J. Mol. Struct.* **1976**, *34*, 197–218. (d) Cyvin, B. N.; Cyvin, S. J.; Hargittai, M.; Hargittai, I. *Z. Anorg. Allg. Chem.* **1978**, *440*, 111–118. (e) Swanson, B.; Shriver, D. F. *Inorg. Chem.* **1970**, *9*, 1406–1421. (f) Amano, T.; Tanaka, K. *J. Mol. Spectrosc.* **1986**, *116*, 112–119. (g) Mills, I. M. *Spectrochim. Acta* **1963**, *19*, 1585–1594.

Figure 1. Raman spectra of *N*-benzylidene-*n*-butylamine (BnBI) and protonated (BnBIH⁺) and deuterated (BnBID⁺) derivatives in CHCl₃ solution. The highest frequency shoulder in the protonated and deuterated species is due to decomposition products.

stretching force constant: case A, for an increase of 0.5 mdyn/Å upon complexation and rehybridization as we calculate in the following paper, and case B, for a decrease of 0.3 mdyn/Å upon complexation. This approach makes possible a comparison of these differing views of the effect of complex formation.

To our knowledge, there is no force field available for an imine–BF₃ complex. Therefore, the force field used for this species was the same as that used for the protonated derivative with the modifications that the N—B stretch and the C=N—B bend were fixed at 3.85 mdyn/Å and 0.5 mdyn Å/rad², respectively. These force constant values are similar to those reported in the literature for the trimethylamine–BF₃ complex,[16c,d] in which the N–B stretching frequency is ~690 cm⁻¹, and for the acetonitrile–BF₃ complex,[16e] in which the above mode appears at 661 cm⁻¹ and the C≡N—B bending motion occurs at ~100 cm⁻¹. The C=N/N—B (stretch/stretch) and the C=N/C=N—B (stretch/bend) interaction force constants were optimized to fit the C=N stretching frequency in the *N*-benzylidene-*n*-butylamine–BF₃ complex. The final matrix elements were 0.53 mdyn/Å for the C=N/N—B (stretch/stretch) and 0.39 mdyn/rad for the C=N/C=N—B (stretch/bend) interaction force constants.

We also performed normal coordinate calculations for methylimine and its protonated species. The ab initio force field calculated by Bot-schwina[16a] was used for the neutral species and modified according to the calculations in the following paper for the protonated derivative. Details may be found in the supplementary material.

Results

Imines. Figure 1 shows Raman spectra of *N*-benzylidene-*n*-butylamine Schiff's base and its protonated and deuterated derivatives in chloroform. The work on benzaldehyde[17] provides assignments for the ring and related vibrational motions (see Table III). Thus, the band at 1696 cm⁻¹, assigned to C=O stretching frequency in benzaldehyde, is shifted upon Schiff's base formation to 1646 cm⁻¹ and is assigned to the C=N stretching frequency.[18] Upon protonation, the frequency of this mode increases to 1680 cm⁻¹ and a new band appears at 1425 cm⁻¹ in Raman and at 1418 cm⁻¹ in IR; this band is absent in the unprotonated and deuterated Schiff's base derivatives and is assigned to the C=N—H bending motion. Deuteration of the Schiff's base increases the C=N frequency mode to 1660 cm⁻¹.

Complexation of benzylidene-*n*-butylamine with BF₃ in dimethyl sulfoxide solution increases the frequency of the C=N stretching mode to 1690 cm⁻¹. Spectra of the neutral and protonated Schiff's base species in this solvent are also shown in Figure 2.

The C=N stretching frequency is sensitive to the nature of the amine used in forming the Schiff's base. For the benzaldehyde

(17) Zwarich, R.; Smolarek, J.; Goodman, L. *J. Mol. Spectrosc.* **1971**, *38*, 336–357.

(18) (a) Parry, K. A. W.; Robinson, P. J.; Sainsburry, P. J.; Waller, M. J. *J. Chem. Soc. B* **1970**, 700–703. (b) Patai, S. *The Chemistry of Carbon Nitrogen Double Bond*; Interscience: New York, 1970; Chapters 1 and 4.
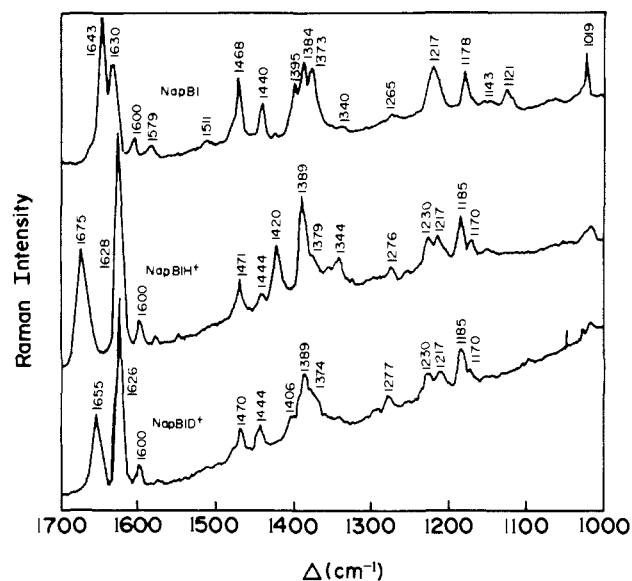
Table III. Frequency[a] Assignments for *N*-Benzylidene-*n*-butylamine (BnBI) and Protonated (BnBIH) and Deuterated (BnBID) Derivatives

BnBI	BnBIH	BnBID	assignments
1002 s	1002 s	1002 s	ν_{12}
1025 m	1030 m	1030 m	ν_{19a}
1060 w	1060 w	1060 w	chain
1114 w			
	1121 w	1121 w	
1159 w			solvent
1170 m	1169 m	1168 m	ν_{9a}
	1194 m	1194 m	
1222 vs	1225 s	1220 s	solvent
1221	1228	1224	PhC=N—R[b]
		1243 m	
1293 w	1294 w	1294 w	CH₂wag chain
	1306 w	1306 w	
1310 w	1312 w	1311 w	ν_3
	1334 w	1334 w	
1340 w			
	1346 w	1351 w	
1378			CH aldehyde
	1425 m		C=N—H bending
1452 w	1451 w	1459 w	ν_{18b}
1495 m	1497 w	1497 w	$\nu_{18?}$
1588 w			ν_{8a}
1602 vs	1603 vs	1602 vs	ν_{8a}
1646 s	1680 s	1660 s	$\nu_{C=N}$

[a] Frequency in cm⁻¹. [b] See Figure 2 (also observed in methylene chloride as solvent, spectrum not shown).
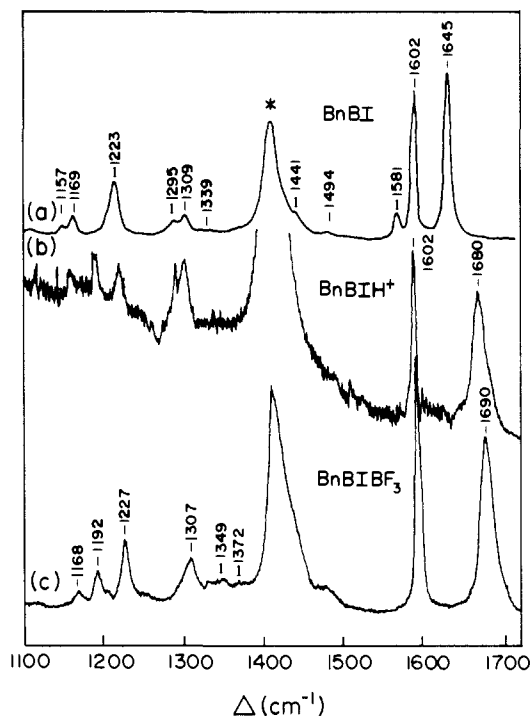
Figure 2. Raman spectra of *N*-benzylidene-*n*-butylamine (BnBI) and protonated (BnBIH⁺) and BF₃ (BnBIBF₃) derivatives in Me₂SO solution. The solvent peaks are denoted by *.

system, substitution of the *n*-butyl group by a methyl group shifts the C=N stretching frequency to 1650 cm⁻¹; upon protonation, this mode increases to 1684 cm⁻¹. The corresponding frequencies for *tert*-butyl substitution are 1640 and 1666 cm⁻¹, respectively (spectra not shown).

The Raman spectra of 2-naphthylidene-*n*-butylamine and its protonated and deuterated Schiff's bases are shown in Figure 3. The C=N stretch increases from 1643 cm⁻¹ (in the neutral species) to 1675 cm⁻¹ upon protonation and to 1655 cm⁻¹ in the deuterated derivative. Similar to the protonated benzaldehyde Schiff's base derivative, the protonated 2-naphthylidene-*n*-butylamine derivative shows a band at 1420 cm⁻¹ in the Raman

Figure 3. Raman spectra of 2-naphthylidene-n-butylamine (NapBI) and protonated (NapBIH⁺) and deuterated (NapBID⁺) derivatives in CHCl₃ solution.

Table IV. Frequency[a] Assignments for N-Naphthylidene-n-butylamine (NAPnBI) and Protonated (NAPnBIH) and Deuterated (NAPnBID) Derivatives.

NAPn BI	NAPnBIH	NAPnBID	assignments
1019 m	1019 w	1019 w	a¹
1121 w			
1143 w	1143 w	1143 w	aⁱⁱ
	1170 w	1170 w	
1178 m			a¹
	1185 m	1185 m	
1217 m	1217 m	1217 m	solvent (CHCl₃)
	1230 m	1230 m	a¹
1265 w			skeletal
	1276 w	1277 w	a¹
1340 w	1344 m		a¹
1373 m	1379 m	1374 m	a¹
1384 s	1389 s	1389 s	a¹
1395 s			a¹
	1420 s		C=N—H bending
1440 m	1444 m	1444 m	a¹
1468 m	1471 m	1470 m	a¹
1511 w	1511 w	1510 w	a¹
1579 w	1579 w	1579 w	a¹
1600 w	1600 w	1600 w	a¹
1630 s	1628 s	1626 s	a¹
1643 s	1675 s	1655 s	C=N stretching

[a] Frequency in cm⁻¹.

spectrum which is absent in the spectra of the unprotonated and deuterated species. The BF₃ complex of the above species also shows an increased C=N vibrational frequency (to 1683 cm⁻¹, spectrum not shown). Table IV shows the assignments for the observed vibrational frequencies; the work on naphthalene[19] and naphthaldehydes[20] have been used for the main assignments. We have also recorded vibrational spectra for Schiff's base species in a series of anthracene derivatives (spectra not shown). Protonation of 9-anthrylidene-n-butylamine increases the C=N stretching frequency from 1644 to 1663 cm⁻¹ (Table VIII).

Linear polyene Schiff's bases are well-known to exhibit behavior analogous to that observed for the aromatic Schiff's bases: upon protonation the C=N stretching frequency increases.[3] The Raman data in Figure 4 show that the analogy extends to the trans-retinal Schiff's base–BF₃ complex as well. Figure 4a shows
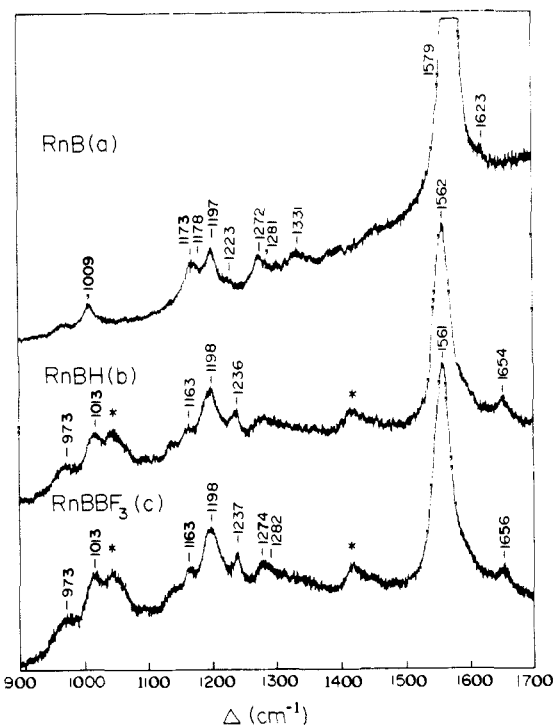
(19) Grofcsik, A.; Kubinyi, M.; Fogarasi, G. J. Mol. Struct. 1982, 89, 63–70.

(20) Sharma, O. P.; Singh, S. N.; Singh, R. D. Indian J. Phys. 1974, 48, 494–503.

Figure 4. Resonance Raman spectra of retinylidene-n-butylamine (RnB) and protonated (RnBH⁺) and BF₃ (RnBBF₃) derivatives im Me₂SO solution. The solvent peaks are denoted by *.

Table V. Chemical Shift for Carbonyl and Imine Protons of the Kind:[a]

Ar	substituent	H_a	α-CH₂
C₅H₅[b]	carbonyl	10.08	
	imine	8.30 (s)	3.65 (t)
	prot imine	9.38 (d)	4.10 (q)
	deut imine	9.38 (s)	4.10 (t)
C₁₀H₈[c]	carbonyl	10.04 (s)	
	imine	8.30 (s)	3.60 (t)
	prot imine	8.8 (s)	3.95 (b)
	deut imine	8.7 (s)	3.95 (t)
C₁₄H₁₀[c]	carbonyl	11.32 (s)	
	imine	9.28 (s)	3.86 (t)
	prot imine	9.75 (b)	4.29 (b)

[a] R = propyl group; s = singlet; d = doublet; t = triplet; q = quartet; b = broad. [b] 250-MHz NMR. [c] 60-MHz NMR.

the spectrum of the neutral Schiff's base in Me₂SO; the C=N stretch occurs at 1623 cm⁻¹. In the BF₃ complexed retinal Schiff's base derivative (Figure 4c), the C=N stretching mode occurs at 1656 cm⁻¹. A more detailed account of the reaction of linear polyene Schiff's bases with Lewis acids is presented elsewhere.[9c,d]

The NMR spectra recorded for benzaldehyde Schiff's bases and their protonated and deuterated forms are presented in Figure 5. Table V collects the NMR chemical shift data for the H(a) and α-CH₂ protons of N-benzylidene-n-butylamine, 2-naphthylidene-n-butylamine, and 9-anthrylidene-n-butylamine and their protonated and deuterated forms. The data indicate, in agreement with similar studies,[4a,21] that a downfield shift of the H(a) and α-CH₂ protons occurs upon protonation or deuteration of the aromatic Schiff's bases. The splitting of the H(a) proton into a doublet and of the α-CH₂ into quartet is due to the H(b) proton present on the imine nitrogen. As expected, these features are absent in the unprotonated and deuterated Schiff's bases where

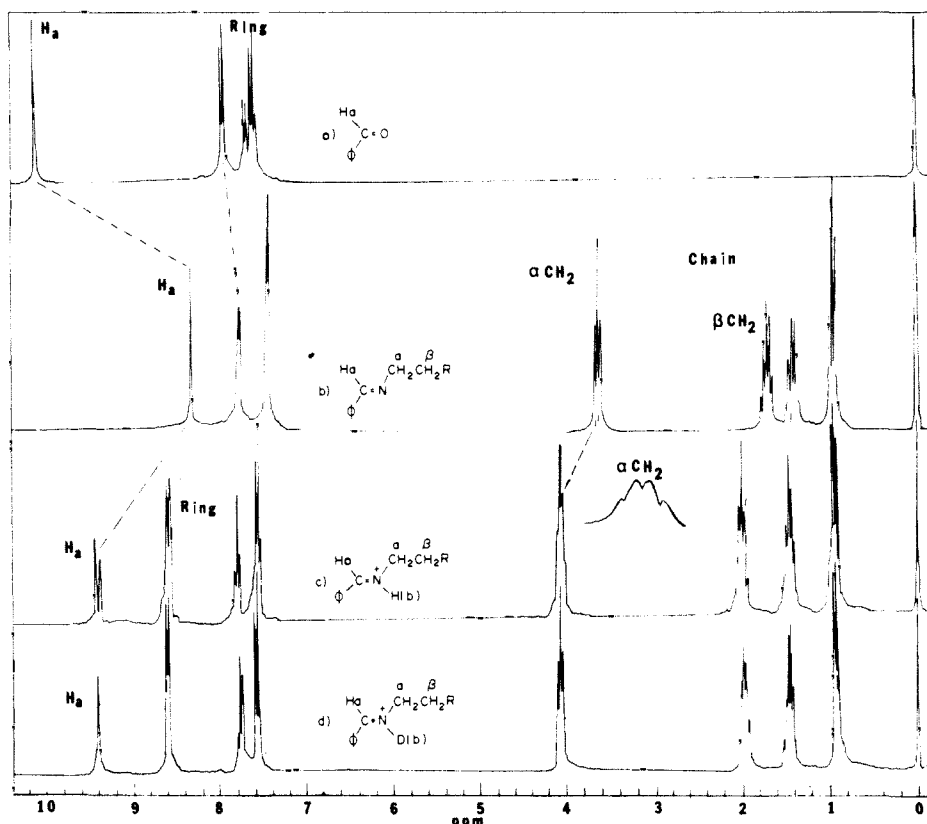(21) Sharma, G. M.; Roels, O. A. J. Org. Chem. 1973, 38, 3648–3651.

Figure 5. NMR spectra (250 MHz) of benzaldehyde (a), *N*-benzylidene-*n*-butylamine (b), and its protonated (c) and deuterated (d) derivatives in CDCl₃ solution.

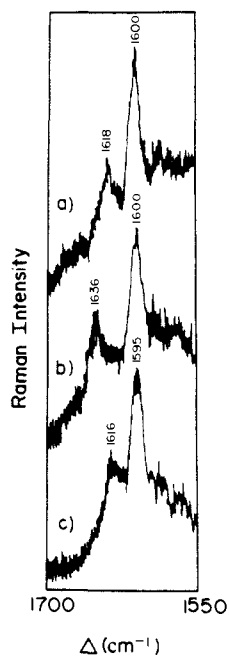**Figure 6.** Raman spectra of α-phenylbenzylidene-*n*-butylamine (a) and protonated (b) and deuterated (c) derivatives in methanol solution.

the (Ha) proton gives a singlet and the α-CH₂ protons appear as triplet.

Ketimines. Figure 6 shows high-frequency Raman spectra for the α-phenylbenzylidene-*n*-butylamine system, $(C_6H_5)_2C=N-(CH_2)_3CH_3$. For the neutral species (Figure 6a), the C=N stretching frequency appears at 1618 cm⁻¹; upon protonation (Figure 6b) or deuteration (Figure 6c), this mode is shifted to 1636 or to 1616 cm⁻¹, respectively. Figure 7 shows Raman spectra for a second ketimine system: α-phenylbenzylideneamine, $(C_6-H_5)_2C=NH$. The spectra of the parent ketone, benzophenone,
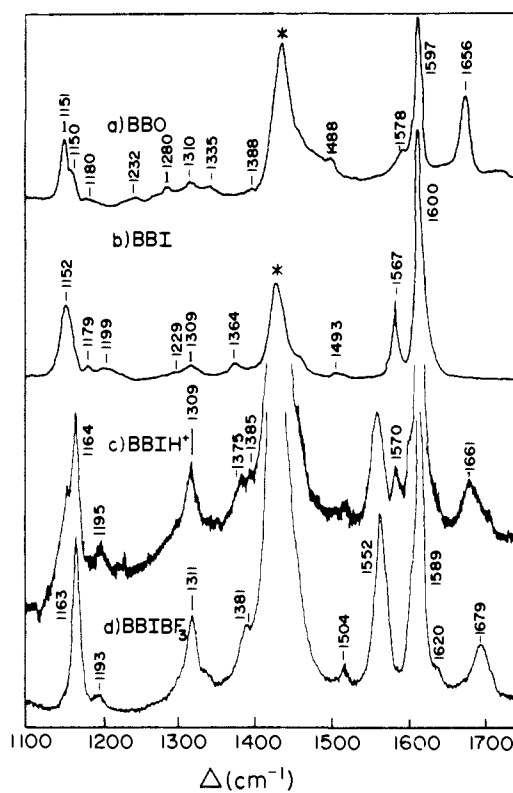
Figure 7. Raman spectra of benzophenone (BBO), α-phenylbenzylideneamine (BBI), and protonated (BBIH⁺) and BF₃ (BBIBF₃) derivatives in Me₂SO solution. The solvent peaks are denoted by *.

is shown in Figure 7a. The C=N stretching occurs at 1600 cm⁻¹ and the C=N—H bending mode appears at 1364 cm⁻¹ in the neutral Schiff's base (Figure 7b). These assignments are based on the isotope studies carried out by Datin et al.[22] Protonation

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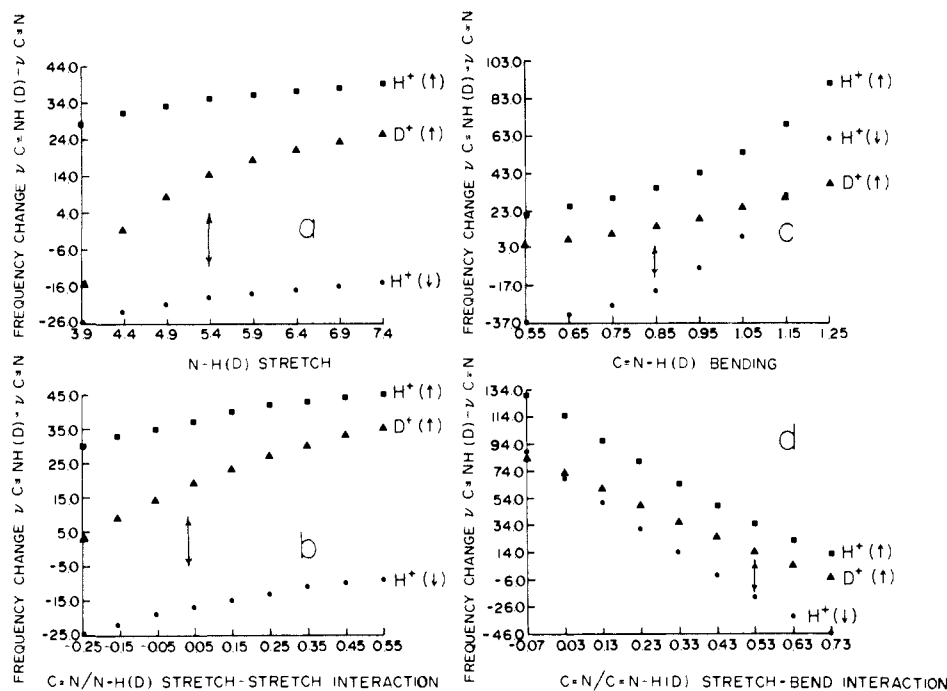
Figure 8. Change in the C=N stretching frequency between the protonated and unprotonated models for an increase [H(↑)], [D(↑)] (from 10.60 to 11.10 mdyn/Å) or decreace [H(↓)] (from 10.60 to 10.30 mdyn/Å) in the C=N stretching force constant of the protonated and deuterated species as a function of (a) N—H(D) stretch; (b) C=N/N—H(D) stretch-stretch; (c) C=N—H(D) bending; (d) C=N/C=N—H(D) stretch-bend.

(Figure 7c) increases the C=N stretching mode to 1661 cm^{-1}, and in the BF$_3$ complex (Figure 7d) this mode is shifted to 1679 cm^{-1}.

Vibrational Analysis. Table VI shows the C=N stretching frequency and the potential energy distribution (PED) calculated for the model structures according to the force fields in Table II. The C=N vibration of the unprotonated species occurs at 1645 cm^{-1}. For this mode, the C=N stretching force constant contributes 92% to the PED; the remaining contributions involve mainly the N-C and C-C stretch and the C-C-H bending modes. The normal mode composition of the C=N stretching frequency in Table VI is very similar to that reported recently for a series of simple imines.[15a,b,d]

In the protonated species the C=N stretching frequency occurs at 1680 cm^{-1} with an 89% contribution from the C=N stretching force constant. Other contributions involve the same modes present in the nonprotonated species plus a 5% contribution from the C=N—H bending motion. The contribution from the bending motion was expected since the force field for the protonated model was optimized to reproduce a C=N—H bending frequency between 1425 and 1420 cm^{-1} as observed experimentally for N-benzylidene-n-butylamine and 2-naphthylidene-n-butylamine (see Figures 1-3). Other molecules, such as allylimine (CH$_2$=C-H—CH=NH) in which the C=N—H bending motion occurs at 1368 cm^{-1}, show no involvement of the bending mode in the C=N stretching frequency.[15b]

Because the normal coordinate analyses for the neutral and protonated Schiff's bases are reasonably well-constrained by the force constant values in Table I, we have carried out further calculations to investigate the behavior of the C=N linkage. Figure 8 shows the difference between the C=N stretching frequency in the protonated and neutral Schiff's base, CH$_3$CH= NCH$_3$, as a function of the force constants of the principal modes which contribute to the PED. As noted in the Methods section, the calculations were carried out for both rehydrization model and stretch/bend interaction model scenarios. For the former we used our calculated increase of 0.5 mdyn/Å in the C=N force constant upon protonation (case A, denoted as [H$^+$(↑)]); for the latter we allowed the C=N force constant to decrease by 0.3 mdyn/Å upon protonation (case B, denoted as [H$^+$(↓)]). Also

(22) Perrier-Datin, A.; Lebas, J. M. *Spectrochim. Acta Part A* **1969**, *25*, 169-185.

Table VI. C=N Stretching Frequency of Model Structures[a]

structure[b]	C=N (cm^{-1})	PED[c]	Δ[d] (cm^{-1})
RHC=NR	1645	92(C=N), 9(C=C), 4(C=H), 4(HCN)	
RHC=^{15}NR	1625	91(C=N), 11(C—), 5(C—H), 4(HCN)	20 (u)
[RHC=NHR]$^+$	1680	89(C=N), 10(C=C), 6(HCN), 5(N—C), 5(CNH)	35 (u)
[RHC=NDR]$^+$	1659	84(C=N), 6(C—C), 6(N—C), 4(CND)	21 (p)
[RDC=NHR]$^+$	1664	85(C=N), 10(C-C), 4.5(DCN), 5(N—C), 6.8(CNH)	16 (p)
[RHC=^{15}NHR]$^+$	1660	84(C=N), 10(C—C), 7(HCN), 4(N—C), 6(CNH)	20 (p)
RHC=N(BF$_3$)R	1691	94(C=N), 8(C—C), 4.5(HCN), 4(N—C)	46 (u)

[a] Calculation based on force field, Table II. [b] R = CH$_3$ group. [c] PED, potential energy distribution; major internal coordinate contribution in the calculation was 100%. [d] Δ, difference in the C=N stretching frequency of the indicated compound relative to the unprotonated (u) or protonated (p) species.

shown are calculations for the deuterated Schiff's base for the rehybridization model, case A [D$^+$(↑)]. Indicated in each panel is the value used for the particular force constant from our constrained normal coordinate analysis (Tables I and II). From the slopes of the curves near these values, these plots provide an indication as to how the ν(C=N) frequency is influenced by the force constants of the various relevant modes. For both cases A and B, Figure 8 (a and b) shows that the N—H stretch and C=N/N—H stretch/stretch interaction force constants are unlikely to lead to the observed increase in ν(C=N) upon protonation. Figure 8 (c and d) shows that the dependence of ν(C=N) on the C=N—H bending and C=N/C=N—H stretch/bend interaction force constants is more pronounced. For case B [H$^+$(↓)], for example, Figure 8d shows that ν(C=N) increases by ~68 cm^{-1} when a force constant of 0.03 mdyn/rad is used for the C=N/C=N—H stretch/bend interaction term. Figure 8c shows for case B that a bending force constant of 1.15 mdyn Å/rad^2 leads to an increase of ~31 cm^{-1} in the C=N stretching

frequency. These observations suggest that a small stretch/bend interaction term in conjunction with a relatively high bending force constant could account for the ~ 35-cm^{-1} increase in the C=N stretching frequency in the case where the stretching force constant is assumed to decrease upon protonation. However, in allylimine, (CH_2=CH—CH=NH), the simplest form of an alkene–imine conjugated π system, the bending force constant is 0.86 mdyn Å/rad^2 and the stretch/bend interaction force constant is reported to be 0.58 mdyn/rad.[15b] These values appear to be typical for this class of compounds (see Table I). Figure 8d shows that a stretch/bend interaction force constant in this range is unable to account for the increase in ν(C=N) in the case B [$H^+(\downarrow)$] situation. If the force constant increases upon protonation, as our calculations indicate, then a stretch/bend interaction of this magnitude reproduces the observed C=N frequency (Figure 8d) under conditions when the other force constants are within constraints imposed by Table I. This suggests that the increased C=N force constant we calculate for the protonated Schiff's base plays a more important role in increasing ν(C=N) than does the stretch/bend interaction force constant. Similar conclusions regarding the bending force constant are indicated by Figure 8c.

For case A, Figure 8 also shows that the deuterium isotope shift for the protonated Schiff's base is not linear with a change in force constants of the C=N—H fragment. This is apparent for all four of the force constants in Figure 8, but the difference in slopes for the [$H^+(\uparrow)$] and [$D^+(\uparrow)$] plots at their calculated, Table II values, is most pronounced for the N–H(D) stretch (Figure 8a) and the C=N/N—H(D) stretch/stretch (Figure 8b) interaction force constants.

Analogous calculations for the BF_3 derivative showed that the dependencies of ν(C=N) on C=N—BF_3 vibrational parameters are generally attenuated relative to those of the C=N—H(D) group in Figure 8. The C=N/N—BF_3 stretch/stretch interaction, which is somewhat similar to the C—C/C—CH_3 stretch/stretch interaction that increases the C—C frequency in methylated linear polyenes,[3j] did produce a comparable shift in ν(C=N) (~ 7 cm^{-1} when varied from 0.73 to 0.03 mdyn/Å), but this appears to be too modest to account for both a decrease in C=N force constant and a 50–80-cm^{-1} increase in ν(C=N). The attenuated dependence on C=N—BF_3 parameters contrasts with the more pronounced ν(C=N) increase upon BF_3 complex formation (e.g., for benzaldehyde, protonation increases ν(C=N) by 35 cm^{-1}, whereas BF_3 complex formation leads to an increase of 45 cm^{-1}). Thus, even though there is uncertainty in the BF_3 force field, as noted in the Methods section, a reasonable set of force constants that includes an increase in the C=N stretching force constant provides agreement with the experimental data. We conclude, therefore, that the case A scenario most likely applies to these adducts as well.

Discussion

C=N Stretching Frequency: Neutral Schiff's Bases. Table VII summarizes aldehyde and neutral Schiff's base functional group stretching frequencies for a number of linear polyene and aromatic species. For both classes of compounds, conjugation effects are apparent, as increasing the number of double bonds leads to a decrease in the C=O and C=N stretching frequency. This trend is summarized in Figure 9 where the C=O frequency in aromatic aldehydes and the C=N frequency in the corresponding neutral Schiff's base formed by reaction with n-butylamine are plotted as functions of the number of double bonds in the aromatic system. The slopes of the two plots show that conjugation effects are more pronounced for the aldehyde group than for the neutral Schiff's base, most likely the result of the stronger electron-withdrawing character of the carbonyl. For example, increasing the resonance system from benzaldehyde to a formylated metalloporphyrin brings about a change in the C=O stretching frequency of 28 cm^{-1}, whereas the corresponding shift in the Schiff's base analogues is only 7 cm^{-1}. Similar effects are apparent in the optical spectroscopy of these two classes of compounds;[4] that is, the optical spectra of aromatic aldehydes are more strongly red-shifted than those of the corresponding neutral Schiff's bases.

Table VII. Carbonyl and Imine Stretching Frequency of Polyene and Aromatic Compounds

compound	C=O (cm^{-1})	compound	C=N (cm^{-1})
CH_3CHO^a	1715	$(CH_3)_2CHCH$=NCH$(CH_3)_2^h$	1667
CH_3CH=$CHCHO^a$	1690	$CH_3(CH$=$CH)$-CH=NCH-$(CH_3)_2^h$	1658
$CH_3(CH$=$CH)_2CHO^a$	1680	$CH_3CH_2(CH$=$CH)_2CH$=NCH-$(CH_3)_2^h$	1643
$CH_3(CH$=$CH)_3CHO^a$	1678	*trans*-retinal+ hexylamine[b]	1625
trans-retinal[b]	1673	M_{412} chromophore[i]	1620
benzaldehyde[c,d]	1694	*N*-benzylidene-*n*-butylamine[c]	1646
naphthaldehyde[c,e]	1684	2-naphthylidene-*n*-butylamine[c]	1643
anthraldehyde[c]	1677	9-anthrylidene-*n*-butylamine	1644
		$(C_6H_5)HC$=N-$(C_6H_5)^k$	1634
Cu^{2+} porphyrin a^f	1666	Ni porphyrin a^j	1639
$(C_6H_5)_2C$=$O^{c,g}$	1665	$(C_6H_5)_2C$=N-$(CH_2)_3CH_3^c$	1618
		$(C_6H_5)_2C$=N-$(C_6H_5)^k$	1616

[a] Reference 25. [b] Reference 3i. [c] This work. [d] Reference 17. [e] Reference 20. [f] Reference 26. [g] Reference 22. [h] Reference 27. [i] Reference 3a. [j] Reference 4a. [k] Reference 7.
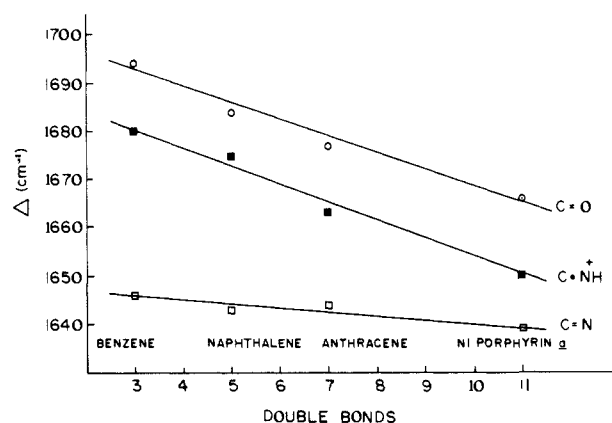
Figure 9. Effect of increasing the aromatic ring conjugation on the characteristic group frequency of aldehydes (○), Schiff's bases (□), and protonated Schiff's bases (■).

When the alkyl amine is replaced by an aromatic amine in the Schiff's base linkage, there is a decrease in the C=N frequency although this effect is still fairly small; for the benzaldehyde system, for example, there is a 12-cm^{-1} difference in the C=N mode for the Schiff's bases formed from n-butylamine and from aminobenzene. A further reduction in the frequency of the C=N stretch (to 1616 cm^{-1}) is observed as the number of substituent phenyl rings is increased to three. These trends indicate that conjugation effects play a role in determining the C=N stretching frequency but that the dependence is fairly weak.

In comparison with the aromatic compounds, it is apparent from Table VII that the linear polyene Schiff's bases show a much stronger relationship between C=N frequency and number of double bonds. Similar behavior has been reported for the neutral nitrile system where the C≡N frequency shows a more pronounced dependence on extent of conjugation in linear unsaturated systems than in analogous aromatic species.[23] For the nitrile system, these conjugation effects were suggested to be the determining factor in accounting for the frequency differences between these two classes of compounds; i.e., the interaction of the

(23) Besnainou, S.; Thomas, B.; Bratož, S. *J. Mol. Spectrosc.* **1966**, *21*, 113–124.

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Table VIII. Changes in the C=N Stretching Frequency upon Complexation with Lewis Acids

complex	CN[a]	ν_{CN^+H}	ν_{CN^+D}	ν_{CNA}	$\Delta\nu_{H^+}$[b]	$\Delta\nu_{D^+}$	$\Delta\nu_A$	δ_{CNH}[c]
PhHCNC₄H₉[d]	1646	1680	1660	1690	34	20	43	1425
Ph₂CNC₄H₉[d]	1618	1636	1616		18	-2		
Ph₂CNH[d]	1600	1661		1679	61		79	1364
NaphCNC₄H₉[d]	1643	1675	1655		32	12		1420
AntCNC₄H₉[d]	1644	1663			19			
PhHCNMe[e]	1658	1695		1712	37		54	
PhHCNPh[e]	1634	1672		1673	38		39	
Ph₂CNMe[e]	1634	1669		1661	35		27	
Ph₂CNPh[e]	1616	1623		1621	7		5	
Bu₂CNH[e]	1610	1670		1672	60		62	
Ni-porphyrin a[f]	1639	1650	1640		11	1		
M₄₁₂[g]	1620							
rhodopsin[g,k]		1655	1630		35	10		
BR₅₇₀[h]		1642	1625		22	5		1350
Br₆₀₃[h]		1641	1623		21	3		1346
HR₅₇₈[i]		1633	1621		13	1		1349
retinylidene-*n*-butylamine[j]	1622	1655	1630		33	8		
retinylidene-*n*-butylamine[d]	1623	1654		1656	31		33	

[a] $\nu_{C=N}$ stretching frequency: protonated (ν_{CN^+H}), deuterated (ν_{CN^+D}), and BF₃ complex (ν_{CNA}). Frequency in cm⁻¹. [b] $\Delta\nu_{H^+} = \nu_{CN^+H} - \nu_{CN}$; $\Delta\nu_{D^+} = \nu_{CND} - \nu_{CN}$; $\Delta\nu_A = \nu_{CNA} - \nu_{CN}$. [c] C=N—H bending mode (δ_{CNH}). [d] This work. [e] Reference 7. [f] Reference 4a. [g] Reference 3a. [h] Reference 3e. [i] Reference 28. [j] Reference 31. [k] Differences in frequency relative to M₄₁₂ chromophore.

C=N π orbital and the π system of the aromatic ring is smaller than its interaction with that of the linear, unsaturated systems. The same phenomenon appears to be in effect in the Schiff's base systems and thus we expect the extent of conjugation to be higher for the C=N group in the linear polyene Schiff's bases than in the aromatic imine Schiff's bases, with the consequent decrease in the C=N stretching frequency of the former.

C=N⁺ Stretching Frequency: Schiff's Base/Lewis Acid Complexes. Table VIII collects data on various Schiff's base–Lewis acid adducts which were studied in the present work or described by other workers. The dependence of the C=N⁺ stretching frequency on the size of the conjugated system in protonated aromatic Schiff's bases is shown in Figure 9. The same type of dependence as noted for aromatic aldehydes and Schiff's bases is observed; as the number of double bonds increases, the C=N⁺ stretching frequency decreases. Moreover, the slope is steeper than in the neutral Schiff's base compounds, probably reflecting the effect of the increased electronegativity of the protonated substituent on the conjugated system.

The data in Table VIII show that the increase in the C=N frequency upon complexation with BF₃ is comparable to that observed upon protonation. Moreover, for both of these Lewis acids (H⁺, BF₃) the largest shifts arise for compounds in which the Schiff's base nitrogen is substituted only by protons whereas the smallest shift occurs for the fully phenyl substituted species. These observations indicate that a common mechanism is likely to be responsible for the increase in the C=N stretching frequency in both cases.

As noted in the Introduction, the increase in frequency upon protonation is counterintuitive. For the protonated Schiff's bases of retinal and its analogues, a C=N/C=N—H stretch/bend interaction model has been invoked to explain this phenomenon. The results we have obtained and a consideration of the similarities between the nitrile system and the Schiff's base system suggest an alternative explanation that invokes a simple strengthening of the Schiff's base C=N bond upon complexation. In the nitrile system, complexation of the nitrogen lone pair by a Lewis acid leads to a decrease in C≡N bond length. For example, in acetonitrile the C≡N bond length is 1.157 Å and decreases by 0.02 Å to 1.137 Å upon complexation by BF₃.[8d] Likewise, a decrease in C≡N bond length is observed upon protonation of HCN.[16f] In both systems, and in nitriles in general, ν(C≡N) increases in the complexed compounds. This suggests that the critical factor in determining ν(C≡N) is the state of the nitrogen lone pair and that complexation leads to a rehybridization such that the C≡N bond strength increases to produce the observed effects.[8c,e] The application of a similar model to the nitrogen lone pair in Schiff's bases and to its reponse to complexation provide a straightforward interpretation of several aspects of the behavior of the C=N bond.

The fundamental determinant of ν(C=N) and its shift upon complexation in this model is the status of the lone pair electrons. Thus this model predicts that the behavior of ν(C=N) will be relatively insensitive to the identity of the complexing species and is able to account for the similar increases in C=N stretching frequency when the lone pair is complexed by either protons or by BF₃. Likewise, the model is consistent with the similar trends noted above for the dependence of the magnitude of the ν(C=N) shift in protonated and BF₃ complexed Schiff's bases upon the other C=N substituents in the various Schiff's bases. The increase in C=N stretching frequency observed by Marcus et al.[31] upon methylation is explained in the rehybridization model without postulating stretch/stretch or stretch/bend interactions within the C=N⁺—CH₃ structure to drive the C=N stretching frequency up. More subtle properties of the Schiff's base linkage are also accounted for by the rehybridization model. For example, the Raman data in Figure 7 show that α-phenylbenzylideneamine (**8**)
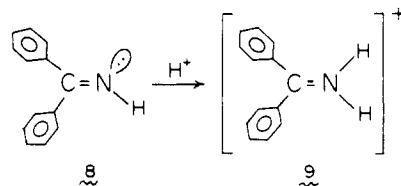
in its neutral form has a C=N stretching frequency at 1600 cm⁻¹ and a C=N—H bending vibration at 1364 cm⁻¹. One might expect in the stretch/bend model that these modes would interact in the neutral species to drive the C=N stretch to higher frequencies. However, the C=N stretch at 1600 cm⁻¹ is lower than the C=N mode in α-phenylbenzylidene-*n*-butylamine (**10**) by 18
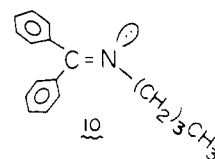
cm⁻¹. Such behavior is difficult to rationalize by the stretch/bend model but does not jeopardize the rehybridization model. Moreover, consistent with the predictions of the rehybridization model, complexation of the lone pair by protonation of **8** to form **9** results in a 61-cm⁻¹ increase in the C=N stretching mode to 1661 cm⁻¹, and BF₃ substitution increases the frequncy of this mode by 79 cm⁻¹.

To analyze the quantitative implications of the rehybridization model we have carried out both ab initio quantum mechanical calculations and normal coordinate analyses. The ab initio calculations were done at the generalized valence bond (GVB) level

for methylimine and protonated methylimine and are given in the following paper. These calculations are consistent with the rehybridization model and show that a decrease in C=N bond length occurs upon protonation. Accompanying this, there is an increase of 0.51 mdyn/Å in the C=N stretching force constant.

We used this increase in the C=N stretching force constant along with well-constrained values for other relevant force constants (see Table I) in carrying out normal coordinate analysis on two different sets of Schiff's base models. For methylimine and methylenimmonium ion (protonated methylimine) the results show (see supplementary material for more details) that an increase in the C=N stretching force constant from 11.14 to 11.64 mdyn/Å increases the C=N stretching frequency upon protonation by 28 cm⁻¹ and upon deuteration by 10 cm⁻¹. For the model structure, CH₃HC=NCH₃, and its derivatives, the same increase of the C=N stretching force constant increases the C=N mode by 35 cm⁻¹ and shifts the deuterium substituted by 21 cm⁻¹. These values are typical of those observed experimentally (Table VIII). Moreover, the calculated frequencies in Table VI for various isotopically substituted imines follow the same trend as those measured experimentally by Mathies and co-workers[3j] and Bagley et al.[3m] in their extensive study of protonated retinal Schiff's bases. Their results[3j] show that deuteration of the Schiff's base nitrogen produces a 23-cm⁻¹ shift in the C=N stretching frequency, and we calculated a 21 cm⁻¹ decrease in close agreement with our experimental result. Deuteration at the carbon of the protonated retinal is observed[3j,m] to decrease the C=N stretching frequency between 12–15 cm⁻¹, and Table VI shows that the calculated decrease for this substitution is 16 cm⁻¹. Substitution by ¹⁵N produces a 14-cm⁻¹ decrease in the C=N stretching frequency in *trans*-retinylidene-*n*-butylamine.[3j] In their calculations, Mathies and co-workers[3j] obtained an 18-cm⁻¹ shift for the ¹⁵N substituted protonated species; we calculated a 20-cm⁻¹ shift for both the unprotonated and protonated derivatives. The shift observed upon deuteration of the Schiff's base nitrogen has been used as an argument in support of the stretch/bend interaction model.[3b,k] But, as Figure 8 indicates, this shift is also dependent upon the N—H (stretch), C=N/N—H (stretch/stretch) and C=N—H (bend) force constants and suggests that their inclusion in the force field representing a protonated Schiff's base, in as constrained a manner as possible, is necessary.

The calculations summarized in Figure 8 and the recent results collected in Table I also provide some insight into previous force fields which were used and the normal coordinate analysis which resulted for Schiff's base species. For example, Aton et al.[3b] used a relatively low value for the C=N stretching force constant (8.1 mdyn/Å) and a negative stretch/bend interaction force constant (−0.2 mdyn/rad) to produce a protonated retinal Schiff's base C=N stretching frequency of 1659 cm⁻¹. It is apparent from Figure 8 that the negative interaction force constant will compensate for the low stretching force constant and push the stretching frequency up. Similarly, Kakitani et al.[3k] calculated C=N stretching frequencies of 1659 and 1657 cm⁻¹ for the protonated retinal Schiff's base and for rhodopsin, respectively. For the protonated retinal model they used a C=N stretching force constant of 9.7 mdyn/Å and a stretch/bend interaction constant of 0.2 mdyn/rad. The C=N—H bending force constant was used as a parameter to fit the C=N stretching frequency and they obtained a value of 0.6 mdyn Å/rad². For rhodopsin, they used a smaller C=N stretching force constant (9.3 mydn/Å) and a negative stretch/bend interaction constant (−0.1 mdyn/Å); the bending force constant (0.5 mdyn Å/rad²) was again optimized to reproduce the 1657-cm⁻¹ rhodopsin C=N stretching frequency. Figure 8 indicates that the difference in bending force constants in these two calculations, 0.1 mdyn Å/rad², will not strongly influence the results. Our calculations suggest, however, that the 0.4-mdyn/Å decrease in the stretching force constant used by Kakitani et al.[3k] for rhodopsin relative to the protonated model Schiff's base is compensated by the decrease (by 0.3 mdyn/rad) they assumed in the stretch/bend interaction force constant and that this leads to the similarity in calculated values of ν(C=N) in the two compounds.

In our normal coordinate analysis of the methyl-substituted Schiff's base we used a C=N/C=N—H stretch bend interaction force constant of 0.53 mdyn/rad, a value that is similar to the interaction terms compiled in Table I. To provide some physical insight into this positive value, it is useful to note that the values in Table I are for neutral Schiff's bases. Upon protonation we expect a change in C=N—H bond angle and N–H bond length. Mills notes that changes of interbond angle will produce changes in hybridization for the central atom owing to orbital following of the bending coordinate.[16g] For situations in which bond angle increases lead to greater s content in the bond and hence to shorter bond lengths, a positive value for the stretch/bend interaction force constant is expected. This appears to be the case for the Schiff's base linkage as Eades et al.[15f] have calculated that the C=N—H bond angle increases by 11° and the N—H bond length decreases by 0.008 Å upon protonation of methylimine. In our own calculations we find an increase in the nitrogen s character in the N–H bond in methylimine upon protonation.[9a] These arguments suggest that the C=N/C=N—H interaction force constant will be positive and relatively large in the protonated species, in agreement with the value we have used. These arguments also indicate that hydrogen bonding to the protonated Schiff's base, to the extent that it alters the hybridization at the nitrogen, the C=N—H bond angle, and the C=N and N—H bond lengths, will have strong effects on the C=N stretching frequency. A recent example of such a situation may be the work on pyridoxal Schiff's bases[2d,e] which shows a C=N stretching frequency at 1646 cm⁻¹ and a vibration at 1465 cm⁻¹ with contributions from the C=N—H bending mode. In this particular case, the imine proton is intramolecularly hydrogen bonded to a nearby oxygen which constrains the system and likely perturbs the force constants associated with the C=N—H group. We are in the process now of carrying out calculations to assess the effects of such hydrogen bond interactions on the vibrational properties of the Schiff's base moiety.

In conclusion, the results of our analysis above indicate that the behavior of the nitrogen lone pair is involved in determining the properties of the C=N vibrational mode; changes in the electronic environment of this lone pair, upon protonation or reaction with a Lewis acid, affect the electron density distribution in the C=N linkage. The latter statement is supported by the NMR data shown in Figure 5 and Table V which suggest, in agreement with previous results,[4a,21] that an increase in the electronegativity of the nitrogen occurs upon protonation of Schiff's bases. The protonation of a Schiff's base seems to be analogous to the situation which occurs when a proton is brought up to NH₃ to give NH₄⁺. The lone pair electrons forming the new N–H bond will not stay unaltered in this sp² hybrid orbital; neither will they be equally shared between N and H.[24] In fact, our ab initio calculations at the GVB level show that a reorganization of the s character of the nitrogen lone pair occurs upon protonation such that the s character of the nitrogen in the C=N bond increases.[9a] This change in hybridization produces the shorter C=N bond length and greater C=N stretching force constant, relative to the neutral Schiff's base, which we have used in the above calculations. These concluding remarks indicate the important role of electronic effects in determining the C=N stretching frequency in protonated Schiff's bases and are considered in more detail in the following paper.

(24) Brown, R. D.; Penfold, A. *Trans. Faraday Soc.* **1957**, *53*, 397–402.
(25) Yanovskaya, L. A.; Kryshtal, G. V.; Yakovlev, I. P.; Kucherov, V. F.; Simkin, B. Y.; Bren, V. A.; Minkin, V. I.; Osipov, O.; Tumakova, I. A. *Tetrahedron* **1973**, *29*, 2053–2064.
(26) Babcock, G. T.; Callahan, P. M. *Biochemistry* **1983**, *22*, 2314–2318.
(27) Favrot, J.; Vocelle, D.; Sandorfy, C. *Photochem. Photobiol.* **1979**, *30*, 417–421.
(28) Alshuth, T.; Stockburger, M.; Hegemann, P.; Oesterhelt, D. *FEBS. Lett.* **1985**, *179*, 55–59.

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

(1) (a) Ottolenghi, M. *Adv. Photochem.* **1980**, *12*, 97–200. (b) Aton, B.; Doukas, A. G.; Narva, D.; Callender, R. H.; Dinur, U.; Honig, B. *Biophys. J.* **1980**, *29*, 79–94. (c) Kakitani, H.; Kakitani, T.; Rodman, H.; Honig, B.; Callender, R. *J. Phys. Chem.* **1983**, *87*, 3620–3628. (d) Birge, R. R.; Murray, L. P.; Pierce, B. M.; Akita, H.; Balogh-Nair, V.; Findsen, L. A.; Nakanishi, K. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 4117–4121.

(2) (a) Smith, S. O.; Pardoen, J. A.; Mulder, P. P. J.; Curry, B.; Lugtenburg, J.; Mathies, R. *Biochemistry* **1983**, *22*, 6141–6418. (b) Rothschild, K. J.; Roepe, P.; Lugtenburg, J.; Pardoen, J. A. *Ibid.* **1984**, *23*, 6103–6109. (c) Smith, S. O.; Myers, A. B.; Pardoen, J. A.; Winkel, C.; Mulder, P. P. J.; Lugtenburg, J.; Mathies, R. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 2055–2059. (d) Dupuis, P.; Corcoran, T. C.; El-Sayed, M. A. *Ibid.* **1985**, *82*, 3662–3664.

(3) (a) Witkop, B.; Beiler, T. W. *J. Am. Chem. Soc.* **1954**, *76*, 5589–5597. (b) Karube, Y.; Ono, Y.; Matsushima, Y.; Ueda, Y. *Chem. Pharm. Bull.* **1978**, *26*, 2642–2648. (c) Ledbetter, J. W. *J. Phys. Chem.* **1982**, *86*, 2449–2451. (d) Benecky, M. J.; Copeland, R. A.; Rava, R. P.; Feldhaus, R.; Scott, R. D.; Metzler, C. M.; Metzler, D. E.; Spiro, T. G. *J. Biol. Chem.* **1985**, *260*, 11671–11678.

(4) (a) Ward, B.; Callahan, P. M.; Young, R.; Babcock, G. T.; Chang, C. K. *J. Am. Chem. Soc.* **1983**, *105*, 634–636. (b) Hanson, L. K.; Chang, C. K.; Ward, B.; Callahan, P. M.; Babcock, G. T.; Head, J. D. *Ibid.* **1984**, *106*, 3950–3958. (c) Ward, B.; Chang, C. K.; Young, R. *Ibid.* **1984**, *106*, 3943–3950. (d) Maggiora, L. L.; Maggiora, G. M. *Photochem. Photobiol.* **1984**, *39*, 847–849.

(5) López-Garriga, J. J.; Babcock, G. T.; Harrison, J. F. *J. Am. Chem. Soc.*, preceding paper in this issue.

(6) (a) Coerver, H. J.; Curran, C. *J. Am. Chem. Soc.* **1958**, *80*, 3522–3523. (b) Gerrard, W.; Lappert, M. F.; Pyszora, H.; Wallis, J. W. *J. Chem. Soc.* **1960**, 2182–2186. (c) Swanson, B.; Shriver, D. F.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 2182–2189. (d) Figeys, H. P.; Geerlings, P.; Berckmans, D.; Van Alsenoy, C. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 721–740.

(7) Milligan, D. E. *J. Chem. Phys.* **1961**, *35*, 1491–1497.

(8) Moore, C. B.; Pimentel, G. C.; Goldfarb, T. D. *J. Chem. Phys.* **1965**, *43*, 63–70.