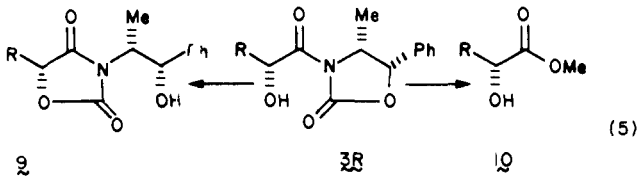
wish to propose that the counterion-dependent product distribution observed in these enolate oxidations could be associated with the intervention and collapse of the hemiaminal **11**. It is relevant that lithium, sodium, and potassium enolates all react rapidly with **4**. However, only the hydroxylation of lithium enolates is complicated by accompanying aldol addition with the product sulfonyl imine **12**.[18] For example, the lithium enolate derived from **1** (R_1 = CH_2Ph) afforded **3R** (54%) as well as 44% of the aldol adduct derived from **12**. In the analogous experiment with the derived sodium enolate, less than 2% of this aldol adduct was observed in competition with hydroxylation. A convincing demonstration that the sulfonyl imine **12** is *not* generated in stoichiometric quantities upon sodium enolate oxidation follows from the reaction of **4** with 2 equiv of the sodium and lithium enolates derived from **1** (R_1 = CH_2Ph) under standard conditions (-78 °C, 5 min). The presence of the second equivalent of enolate was shown in independent experiments to be an effective trap for sulfonyl imine **12**.[18] From these experiments the lithium enolate afforded a 1:1 ratio of hydroxylation and imide aldol adducts while the analogous ratio from the sodium enolate was 85:15. It has been concluded that the sulfonyl imine **12** is *not* stoichiometrically generated in the latter reaction. We speculate that the tetrahedral intermediate **11** (M = Li, Na) may well be involved in the reaction (eq 4) and that the subsequent **11** $\rightleftarrows$ **12** equilibrium is possibly counterion dependent ($K_{eq} > 1$, M = Li, $K_{eq} < 1$, M = Na). Additional experiments to further substantiate this point are being explored.

The final point of interest to the current study has been the development of a reliable procedure for the nondestructive removal of the chiral auxiliary by transesterification without concurrent racemization. Methanolysis of the reported α-hydroxy carboximides may be successfully carried out with 2 equiv of a 0.08 M magnesium methoxide solution in methanol (0 °C, 15 min). The enantiomeric purity of the resultant α-hydroxy methyl esters was determined by subsequent conversion to the (+)- and (-)-MPTA esters[19] which were subjected to capillary gas chromatographic analysis. In the cases reported, this methanolysis procedure affords the derived methyl esters in yields ranging from 80 to 90% with a conservative estimate of less than 0.3% racemization. No detectable level of racemization was seen even in the methanolysis of **3R** (R_1 = Ph) which should be particularly susceptable to enolization. The derived (*R*)-methylmandelate, $[\alpha]_D$ -181.9° (*c* 0.69, C_6H_6) was isolated in 86% yield.[20] One potential problem associated with carboximide methanolysis has been found to be the competing based-catalyzed intramolecular acyl transfer illustrated in the conversion of **3R** to **9** (eq 5).[12] Under the



(5)

conditions described above, this intramolecular acyl transfer is still the prevalent reaction in several of the hindered cases (e.g.: **3R**, R = *t*-C_4H_9; **3S**, R = *i*-C_3H_7).

In conclusion, we have found the asymmetric synthesis of enantiomerically pure α-hydroxy acid synthons via enolate oxidation to be quite general. There are two significant advantages of this protocol (eq 1B) over asymmetric glycolate alkylation (eq 1A). First, enolate oxidation rates with oxaziridine **4** appear to be essentially substrate invariant. Second, α-hydroxy acids inaccessible via the glycolate alkylation route (e.g., **3**, R_1 = Ar) are readily prepared by this method. Finally, during the course of this study we have had the opportunity to compare the relative merits of oxaziridine **4** and MoOPH in stereoselective enolate oxidation. In contrast to observations made by Davis,[9] we have found MoOPH to be slightly more stereoselective and far less reactive than oxaziridine **4**.[21] We estimate that enolate oxidation rates for these two reagents differ by more than 10^{+3}.[22] Overall, the superior yields associated with the oxaziridine reagent render it the reagent of choice.

Acknowledgment. This research has been supported by the National Science Foundation (CHE-8342576) and the National Institutes of Health (GM-33327-02). We also thank the NIH BRS shared instrumentation Grant Program 1 S10 RRoa748-01A1 for work facilities.

Supplementary Material Available: General experimental procedures for hydroxylation and diastereomer analysis as well as ^1H and ^{13}C NMR data for all new compounds prepared (15 pages). Ordering information is given on any current masthead page.

(17) Davis, F. A.; Mancinelli, P. A.; Balasubramanian, K.; Nadir, U. K. *J. Am. Chem. Soc.* **1979**, *101*, 1044.

(18) Such sulfonyl imine aldol adducts can be prepared in quantitative yield from the reaction of **12** with either the sodium or lithium enolates derived from **1** (-78 °C, 5 min).

(19) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

(20) Noe, C. R. *Chem. Ber.* **1982**, *115*, 1591. The reported rotation was $[\alpha]_D$ -176° (*c* 0.83, C_6H_6). See also: Elliott, J. D.; Choi, V. M. F.; Johnson, W. S. *J. Org. Chem.* **1983**, *48*, 2294. Their extrapolated rotation from this study is -182° (*c* 0.8, C_6H_6).

(21) This control experimenta was performed by treating the sodium enolate of **2b** (R_1 = $PhCH_2$) with MoOPH (1.7 equiv, -78 °C, 1.0 h), followed by normal quench and product isolation. The **3R**:**3S** ratio was 2:98 and **3S** (R_1 = $PhCH_2$) was isolated in 37% yield along with 30% of **2b** (R_1 = $PhCH_2$).

(22) Since completing this manuscript the diastereoselective acetoxylation of camphor-based enolates has been reported: Oppolzer, W.; Dudfield, P. *Helv. Chim. Acta* **1985**, *68*, 216.

X-ray Absorption Spectroscopic Studies of the Copper(II) Sites in Bovine Plasma Amine Oxidase

Robert A. Scott*[1] and David M. Dooley*[2]

School of Chemical Sciences, University of Illinois Urbana, Illinois 61801
Department of Chemistry, Amherst College Amherst, Massachusetts 01002

Received December 26, 1984

Primary amines are ubiquitous in nature and have numerous important functions. Oxidative deamination (in which the oxidation of an amine to an aldehyde plus ammonia is coupled to the reduction of O_2 to H_2O_2) is usually the first step in primary amine catabolism.[3] Copper-containing amine oxidases are often found to be the catalysts for this reaction and are also responsible for cross-linking the connective tissue proteins elastin and collagen.[3] These enzymes are composed of two noncovalently bound subunits, containing two Cu(II) ions, with a total M_r ~180 000. The copper site structure and function in amine oxidases are still not very well understood, although the available evidence strongly indicates that copper is essential to catalysis and is probably involved in the reoxidation of the substrate-reduced enzyme by O_2.[3-7] It is known that the amine oxidase Cu(II) sites are tetragonal; EPR param-

(1) University of Illinois.

(2) Amherst College.

(3) (a) Hamilton, G. A. In "Copper Proteins"; Spiro, T. G., Ed.; Wiley: New York, 1981; pp 193-218. (b) Knowles, P. F.; Yadav, K. D. S. In "Copper Proteins and Copper Enzymes"; Lontie, R., Ed.; CRC Press: Boca Raton, FL 1984; Vol. II, pp 103-129.

(4) (a) Barker, R.; Boden, N.; Cayley, G.; Charlton, S. C.; Henson, R.; Holmes, M. C.; Kelly, I. D.; Knowles, P. F. *Biochem. J.* **1979**, *177*, 289-302. (b) Grant, J.; Kelly, I.; Knowles, P.; Olsson, J.; Pettersson, G. *Biochem. Biophys. Res. Commun.* **1978**, *83*, 1216-1224.

(5) (a) Mondovi, B.; Rotilio, G.; Finazzi-Argrò, A.; Vollogini, P.; Malmström, B. G.; Antonini, E. *FEBS Lett.* **1969**, *2*, 182-185. (b) Olsson, B.; Olsson, J.; Pettersson, G. *Eur. J. Biochem.* **1977**, *74*, 329-335. (c) Olsson, B.; Olsson, J.; Pettersson, G. *Eur. J. Biochem.* **1976**, *71*, 375-382.

(6) (a) Dooley, D. M.; Golnik, K. C. *J. Biol. Chem.* **1983**, *258*, 4245-4248. (b) Dooley, D. M.; Cotê, C. E.; Golnik, K. C. *J. Mol. Catal.* **1984**, *23*, 243-253. (c) Dooley, D. M.; Cotê, C. E., unpublished results.

(7) (a) Kelly, I. D.; Knowles, P. F.; Yadav, K. D. S.; Bardsley, W. G.; Leff, P.; Waight, R. D. *Eur. J. Biochem.* **1981**, *114*, 133-138. (b) Yadav, K. D. S.; Knowles, P. F. *Eur. J. Biochem.* **1981**, *114*, 139-144. (c) Rius, F. X.; Knowles, P. F.; Pettersson, G. *Biochem. J.* **1984**, *220*, 767-772.

0002-7863/85/1507-4348$01.50/0

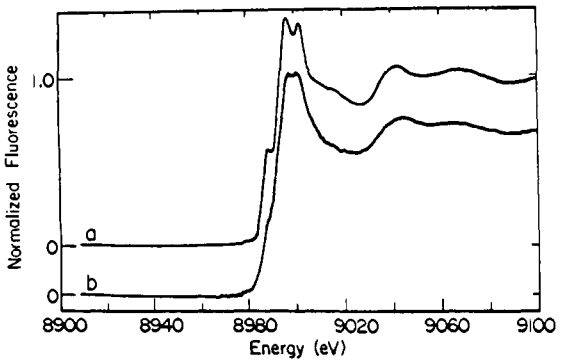


Figure 1. Cu K-edge X-ray absorption spectra of (a) 20 mM aqueous solution of $Cu(imid)_4^{2+}$ and (b) 1.6 mM solution of isolated (oxidized) bovine plasma amine oxidase. Both spectra were recorded as fluorescence excitation data at 4 K and are normalized to unit edge jump by extrapolation of the smooth EXAFS background.

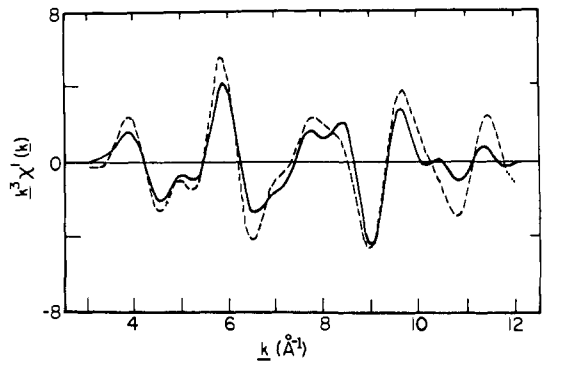


Figure 2. Fourier-filtered Cu EXAFS data for the samples of Figure 1: $Cu(imid)_4^{2+}$ (---) and oxidized amine oxidase (—). The forward Fourier transform (FT) for both data sets ranged from $\underline{k}$ = 3.0 to 12.0 Å^{-1} and the filter window for the back transform (including all FT peaks) was from R' = 0.90 to 3.80 Å with half-Gaussian edges of width 0.20 Å. The amine oxidase EXAFS is virtually identical (except for slightly reduced amplitude) with $Cu(imid)_4^{2+}$ in the low-$\underline{k}$ (3.0–7.0 Å^{-1}) region. Other small differences near $\underline{k}$ = 11 Å^{-1} are probably attributable to the lower signal-to-noise ratio of the protein data.

eters are consistent with primarily nitrogen/oxygen ligands.[4,8] At least one oxygen-donor ligand is probably H_2O.[4] Here we report X-ray absorption spectroscopy (XAS) results that, together with earlier results from other physical methods, permit a reasonable, more detailed model of the Cu(II) site in amine oxidases to be constructed.

Bovine plasma amine oxidase was purified by a published procedure.[9] The enzyme was homogeneous as judged by SDS gel electrophoresis and specific activity measurements. Adventitious copper was removed by extensive dialysis against metal-free EDTA/buffer solutions followed by dialysis against metal-free buffer alone. Enzyme activity was assayed prior to and following the XAS experiments and found to be constant. XAS data on oxidized (as isolated) amine oxidase and $[Cu(imid)_4]^{2+}$ were collected by fluorescence excitation techniques on frozen aqueous solutions at ca. 4 K using an array of NaI(Tl) scintillation detectors.[10] The data were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) on beam line VII-3 during dedicated running at 3.0 GeV and ca. 70 mA. The first shell (Cu–N) Fourier transform peak of the $[Cu(imid)_4]^{2+}$ Cu EXAFS was extracted and complex back transformation used to generate (empirical) amplitude and phase functions.[11] These functions were then used to fit the first shell of the amine oxidase EXAFS, extracted in an identical fashion.

Table I. Curve-Fitting Results for the First Shell of the Cu EXAFS of Bovine Plasma Amine Oxidase

	Cu–N			
compound/protein	R,[a] Å	N	$\Delta\sigma^2$, Å^2	f[b]
$Cu(imid)_4^{2+}$	(2.011)[c]	4	(0)	
amine oxidase	1.99	2	−0.0005	0.471
	1.99	3	+0.0009	0.236
	1.99	4[d]	+0.0030	0.207

[a] R is the Cu–N distance, N is the coordination number, and $\Delta\sigma^2$ is the mean square deviation in R measured *relative* to the model compound ($Cu(imid)_4^{2+}$). [b] f is a χ square error statistic:

$$f = \{\sum_{i=1}^{N}[\underline{k}^3(\chi_{calcd}^{(i)} - \chi_{obsd}^{(i)})]^2/N\}^{1/2}$$

[c] Numbers in parentheses were not optimized. (The values reported for $Cu(imid)_4^{2+}$ are those used to extract the amplitude and phase functions.) [d] Since oxygen as a first-shell scatterer cannot be distinguished from nitrogen, a fit with three N and one O donors will be essentially identical with the fit with four N donors.

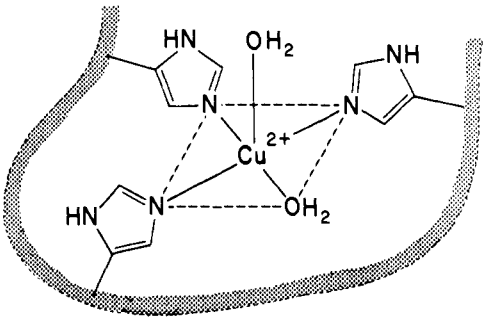


Figure 3. Model for the copper sites in amine oxidases.

Copper K edges for the resting amine oxidase and $Cu(imid)_4^{2+}$ are shown in Figure 1. The similarity between these two spectra is striking. The edge structure is a characteristic signature for imidazole coordination to Cu(II).[12] Although excellent for a protein, the overall resolution in the amine oxidase spectrum is not as good as that in the model complex. This is not uncommon and is attributable to minor heterogeneity in the protein copper sites. One possible source for the broadening could be slightly inequivalent copper sites in the native protein.[13] Nevertheless, the XAS edge data establish that both Cu(II) sites in the amine oxidase are electronically very similar to $Cu(imid)_4^{2+}$. Analysis of the EXAFS region (Figure 2) also suggests a close structural similarity between $Cu(imid)_4^{2+}$ and the amine oxidase Cu(II) sites.[14] First-shell (Cu–N) curve-fitting results are summarized in Table I. An entirely satisfactory fit to the EXAFS data can be obtained with three or four imidazole-like ligands per copper at 1.99 ± 0.02 Å. Structures with less than three imidazole-like ligands are excluded by the data (this requires an unrealistically small Debye–Waller σ^2, and would not reproduce the $Cu(imid)_4^{2+}$ EXAFS), as is sulfur ligation. The EXAFS bond distance is typical for equatorially coordinated imidazoles in tetragonal Cu(II) complexes.[15] Since axial Cu(II) ligands are usually less strongly bound and at substantially longer distances than equatorial ligands, they will not affect the EXAFS fit. Hence the imidazole ligands

(8) (a) Suzuki, S.; Sakurai, T.; Nakahara, A.; Oda, O.; Manabe, T.; Okuyama, T. *FEBS Lett.* **1980**, *116*, 17–20. (b) Yamada, H.; Yasunobu, K.; Yamano, T.; Mason, H. S. *Nature (London)* **1963**, *198*, 1092–1093.

(9) Turini, P.; Sabatini, S.; Befani, O.; Chimenti, F.; Casanova, C.; Riccio, P. L.; Mondovi, B. *Anal. Biochem.* **1982**, *125*, 294–298.

(10) Cramer, S. P.; Scott, R. A. *Rev. Sci. Instrum.* **1981**, *52*, 395–399.

(11) Scott, R. A. *Methods Enzymol.*, submitted for publication.

(12) Co, M. S.; Scott, R. A.; Hodgson, K. O. *J. Am. Chem. Soc.* **1981**, *103*, 986–988.

(13) Mondovi, B.; Sabatini, S.; Befani, O. *J. Mol. Catal.* **1984**, *23*, 325–330.

(14) Our unfiltered data (not shown) are very similar to data reported by Blackburn and co-workers for the Cu,Zn superoxide dismutase and dopamine β-monooxygenase; the copper ions in both proteins also have imidazole and water ligands. See: Blackburn, N. J.; Hasnain, S. S.; Diakun, G. P.; Knowles, P. F.; Binsted, N.; Garner, C. D. *Biochem. J.* **1983**, *213*, 765–768. Hasnain, S. S.; Diakun, G. P.; Knowles, P. F.; Binsted, N.; Garner, C. D.; Blackburn, N. J. *Biochem. J.* **1984**, *221*, 545–548.

(15) (a) Hori, F.; Kojima, Y.; Matsumoto, K.; Oii, S.; Kuroya, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1076–1079. (b) Kojima, Y.; Hirotsu, K.; Matsumoto, K. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3222–3231. (c) Fransson, G.; Lundberg, B. K. S. *Acta Chem. Scand.* **1972**, *26*, 3969–3976.

observed in amine oxidase are probably also equatorial.

Absorbance and EPR data are consistent with such a structure. Ligand-field transitions are in the 19 000–12 000-cm^{-1} range for Cu(II)–imidazole complexes;[16] bovine plasma amine oxidase displays ligand-field bands at 15 150 and 12 500 cm^{-1}.[6c,8a] The EPR parameters for $Cu(imid)_4^{2+}$ are $g_\parallel = 2.267$, $g_\perp = 2.063$, and $A_\parallel = 179 \times 10^{-4}$ cm^{-1},[17] as compared to $g_\parallel = 2.280$, $g_\perp = 2.06$, and $A_\parallel = 155 \times 10^{-4}$ cm^{-1}, for the amine oxidase.[8] Taken together, the data suggest that the structure shown in Figure 3 is an excellent model for the Cu(II) sites in amine oxidases. Magnetic resonance results[4a] and the ligand-substitution chemistry[4,6] of various amine oxidases indicate that H_2O is an equatorial ligand; axially coordinated H_2O has been inferred from ^1H NMR relaxation experiments.[4a] It is possible that the pyridine nitrogen of a pyridoxal derivative[18] or pyrroloquinolinequinone (PQQ)[19] is coordinated to copper. Since a rigid nitrogen heterocycle provides a set of outer-shell scattering atoms similar to imidazole, a structure similar to that shown in Figure 3 but with one imidazole replaced by pyridoxal or PQQ may also be consistent with the XAS data. Extensive XAS experiments designed to elucidate additional Cu(II) structural features in resting amine oxidases and other forms of these enzymes are in progress.

Acknowledgment. This research was supported by grants from the American Heart Association (82-972) and the NIH (GM-27659) to D.M.D., and by a NIH Biomedical Research Support Grant (RR 07030) to R.A.S. We thank Cheryl Snow for technical assistance and Jim Schwartz for help in XAS data collection. The XAS work was performed at SSRL which is supported by the Department of Energy, Office of Basic Energy Sciences, and the NIH, Biotechnology Resource Program, Division of Research Resources.

(16) (a) Bernarducci, E.; Schwindinger, W. F.; Hughey J. L., IV; Krogh-Jesperson, K.; Schugar, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 1686–1691. (b) Schugar, H. J. In "Copper Coordination Chemistry: Biochemical and Inorganic Perspectives"; Karlin, K. D., Zubeita, J., Eds.; Adenine Press: Guilderland, NY, 1983; pp 43–74. (c) McFadden, D. L.; McPhail, A. T.; Garner, C. D.; Mabbs, F. E. *J. Chem. Soc., Dalton Trans.* **1976**, 47–52.
(17) Malmström, B. G.; Vänngard, T. *J. Mol. Biol.* **1960**, *2*, 118–124.
(18) Finazzi-Agrò, A.; Guerrieri, P.; Costa, M. T.; Mondovi, B. *Eur. J. Biochem.* **1977**, *74*, 435–440.
(19) Lobenstein-Verbeek, C. L.; Jongejan, J. A.; Frank, J.; Duine, J. A. *FEBS Lett.* **1984**, *170*, 305–309.

Does Carbon-Protonated Hydrogen Cyanide, H_2CN^+, Exist?

D. J. DeFrees*

Molecular Research Institute
Palo Alto, California 94304

A. D. McLean

IBM Research Laboratory
San Jose, California 95193

Received December 7, 1984

Many theoretical studies of the CH_2N^+ potential energy surface have been performed,[1,2] motivated largely by the postulated role of this molecule in the interstellar synthesis of hydrogen cyanide and hydrogen isocyanide.[3] The most stable isomer is linear $HCNH^+$ corresponding to nitrogen-protonated HCN or, equivalently, carbon-protonated HNC, and which has a heat of formation[4] of 222 ± 4 kcal mol^{-1}. Next is H_2NC^+, nitrogen-protonated HNC, with a heat of formation[5] of 265 ± 9 kcal mol^{-1}, in agreement with the theoretical estimate that H_2NC^+ lies 46 kcal mol^{-1} above $HCNH^+$.[2a] The third isomer, H_2CN^+, carbon-protonated HCN, has been estimated theoretically[2a] to lie 72 kcal mol^{-1} above the linear structure. Moreover, these calculations found it "highly probable" that H_2CN^+ was a saddle point on the potential energy surface and thus not an observable species. Partial evidence was the finding[2a] that H_2CN^+ was a saddle point on the SCF/DZ+P surface. This conflicts with the results of a recent mass spectroscopic experiment.[5] Ions with stoichiometry CH_2N^- were formed from the dissociative electron capture of methylamine. It was postulated that the m/z 28 anions observed were formed by a 1,2-H_2 elimination from the primary product of the electron capture reaction, H_3CNH^-, and that they thus have the H_2CN^- structure. Charge reversal of the m/z 28 anions via kilovolt collisions with helium led to positive ions which were analyzed by collisional activation (CA) mass spectroscopy. The resulting CA spectrum and the vertical nature of the charge reversal reaction[6] indicated that the m/z 28 cation had the H_2CN^+ structure and that this species therefore exists in a potential well. No evidence for ions with this structure was found in experiments with positive ions only.[5,7]

Table I. Theoretical Values of the Lowest Vibrational Frequency of H_2CN^+ (cm^{-1})

basis set	SCF	MP2	CID
6-31G(d)	416	495*i*	
6-31G(d,p)	376	530*i*	281*i*
D95(d,p)	366		
6-311G(d,p)	310	590*i*	
6-311++G(d,p)	312		
6-311G(2d,2p)	297		
6-311G(d,pd)	291		

Preliminary calculations of ours had shown that H_2CN^+ was, in fact, a minimum on the SCF/DZ+P surface, contradicting the earlier calculation.[2a] This and the reported laboratory detection[5] necessitate a theoretical reexamination of the stability of C-protonated HCN. The extended calculations, including electron correlation, reported here show that H_2CN^+ is at a saddle point on the potential energy surface and that it is probable that the charge reversal of H_2CN^- results in the production of H_2CN^+ in an excited triplet state.

To determine whether H_2CN^+ is a minimum or a saddle point structure we have optimized its geometry in C_{2v} symmetry and computed the harmonic vibrational frequencies. If the molecule is at a minimum the frequencies will all be real whereas if it is at a saddle point one of the frequencies will be imaginary. The frequency calculations were done analytically at the SCF level[8] with a sequence of basis sets of increasing size and at the correlated MP2 and CID levels via numerical differentiation of analytic first derivatives.[8,9] The resulting values of the lowest vibrational frequency, the in-plane CH_2 wag, are given in Table I. At the SCF level, C-protonated HCN is a minimum-energy structure with all of the basis sets considered. Thus, extension of the 6-31G(d) (also denoted 6-31G*)[10] polarized split-valence basis

(1) (a) DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; McLean, A. D., manuscript in preparation. (b) Allen, T. L.; Goddard, J. D.; Schaefer, H. F., III. *J. Chem. Phys.* **1980**, *73*, 3255.
(2) (a) Conrad, M. P.; Schaefer, H. F., III. *Nature (London)* **1978**, *274*, 456. (b) Schaefer, H. F., III. *Acc. Chem. Res.* **1979**, *12*, 288.
(3) (a) Herbst, E.; Klemperer, W. *Astrophys. J.* **1973**, *185*, 505. (b) Watson, W. D. *Ap. J.* **1974**, *188*, 35.

(4) On the basis of the relative proton affinity of HCN ((a) Wolf, J. F.; Staley, R. H.; Koppel, I.; Taagepera, M.; McIver, R. T., Jr.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5417), an absolute proton affinity of 205 ± 2 kcal mol^{-1} for ammonia ((b) Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 4329) and values from: (c) Stull, D. R.; Prophet, H. "JANAF Thermochemical Tables", 2nd ed.; National Bureau of Standards: Washington, DC, 1971; NSRDS-NBS 37.
(5) Burgers, P. C.; Holmes, J. L.; Terlouw, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 2762.
(6) (a) Fournier, P. G.; Appell, J.; Fehsenfeld, F. C.; Durup, J. *J. Phys. B* **1972**, *5*, L58. (b) Fehsenfeld, F. C.; Appell, J.; Fournier, P.; Durup, J. *J. Phys. B.* **1973**, *6*, L268. (c) Bowie, J. H.; Blumenthal, T. *J. Am. Chem. Soc.* **1975**, *97*, 2959. (d) McClusky, G. A.; Kondrat, R. W.; Cooks, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 6045.
(7) McLafferty, F. W.; McGilvery, D. C. *J. Am. Chem. Soc.* **1980**, *102*, 6189.
(8) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem. Symp.* **1979**, *13*, 225.
(9) Krishnan, R.; Schlegel, H. B.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4654.

0002-7863/85/1507-4350$01.50/0