observed in amine oxidase are probably also equatorial.

Absorbance and EPR data are consistent with such a structure. Ligand-field transitions are in the 19000-12000-cm^{-1} range for Cu(II)-imidazole complexes;[16] bovine plasma amine oxidase displays ligand-field bands at 15150 and 12500 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.; Mondovì, 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

set by the addition of p-polarization functions on hydrogen decreases the magnitude of the frequency from 416 to 376 cm^{-1}. This is substantially identical with the result obtained with the polarized Dunning (9,5) double-ζ basis D95(d,p).[11] The addition of a third set of valence s and p functions (6-311G(d,p))[12] leads to a further decrease of 66 cm^{-1} in the vibrational frequency to 310 cm^{-1}. Neither the addition of diffuse functions (6-311++G(d,p)),[13] a second set of polarization functions (6-311G(2d,2p)),[14] nor d functions on hydrogen (6-311G(d,pd))[14] leads to a significant change in the frequency. This sequence leads us to conclude that, at the basis set limit, H_2CN^+ is a relative minimum on the potential energy surface. However, at the correlated MP2 level of theory, H_2CN^+ is a saddle point on the potential surface as indicated by the imaginary frequencies in Table I. Note that increasing basis set size works in the same direction at both the SCF and correlated levels. At the SCF level increasing the size of the basis decreases the magnitude of the real frequency whereas at the MP2 level it increases the magnitude of the imaginary frequency, making it likely that even larger basis sets would favor the conclusion that C-protonated HCN is at a saddle point rather than at a minimum. Configuration interaction frequencies including all double excitations (CID is correct to third order in the perturbation theory expansion[15]) were computed with the 6-31G(d,p) basis. As with geometries,[16] MP2 overestimates the correlation correction to the vibrational frequency and the CID answer lies between the SCF and MP2 values and is imaginary by a significant magnitude.

The possibility that higher order correlation terms would change the conclusion that H_2CN^+ is at a saddle point is negligible, and even if they did the barrier to isomerization to the linear isomer would be too small to allow detection of the C-protonated isomer. (At the MP2/6-311++G(d,p) level of theory the vertical charge reversal reaction leaves H_2CN^+ excited by 5 kcal mol^{-1}.) A possible explanation for the collisional activation results is that the charge-reversal reaction produces an excited-state triplet species. It has been shown theoretically[1] that the H_2CN^+ structure is a stable minimum on the triplet potential energy surface and that it is ~120 kcal mol^{-1} above the linear singlet structure. Furthermore, there is precedent for the production of electronically excited cations by the charge reversal reaction.[17] Indeed, the production of triplet methoxy cations, H_3CO^+, from methoxide[17b] provides a close analogy as singlet H_3CO^+ is not a stable minimum on the CH_3O^+ potential surface.

The qualitative similarities between the CH_2N^{+1} system and the $C_2H_4N^{+}$[18] system should be noted here. Both hydrogen cyanide and methyl cyanide protonate only on the terminal nitrogen atom and not on the nitrile carbon. The only stable isomer of $C_2H_4N^+$ corresponding to protonated CH_3CN is CH_3CNH^+; the C-protonated form is a saddle point on the potential energy surface as is the C-protonated form of HCN considered in this paper. By contrast, hydrogen isocyanide and methyl isocyanide both have stable protonated isomers resulting from protonation at either the terminal carbon or the isonitrile nitrogen.

Acknowledgment. This research was supported by NASA Ames Grant NAG 2-16 to D.J.D.

Registry No. H_2CN^+, 53518-13-1.

(10) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
(11) (a) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. (b) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.
(12) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.
(13) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.
(14) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.
(15) Pople, J. A.; Seeger, R.; Krishnan, R. *Int. J. Quantum Chem., Symp.* **1976**, *11*, 149.
(16) DeFrees, D. J.; Raghavachari, K.; Schlegel, H. B.; Pople, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 5576; **1983**, *105*, 3745.
(17) (a) Holmes, J. L.; Szulejko, J. E. *Chem. Phys. Lett.* **1984**, *106*, 292. (b) Burgers, P. C.; Holmes, J. L. *Org. Mass Spectrom.* **1984**, *19*, 452.
(18) DeFrees, D. J.; McLean, A. D.; Herbst, E. *Ap. J.*, in press.

Unprecedented C–N Bond Formation. Crystal and Molecular Structure of N-(2-Aminoethyl)-N-(4-aza-6-aminohexyl)-(α,α-diaminomalonato)cobalt(III) Perchlorate

Morio Yashiro,[1] Akira Shimada,[1] Takeshi Usui,[1] Shigenobu Yano,*[1] Kimiko Kobayashi,[2] Tosio Sakurai,[2] and Sadao Yoshikawa*[1]

The Department of Synthetic Chemistry Faculty of Engineering, The University of Tokyo Hongo, Bunkyo-ku, Tokyo 113, Japan The Institute of Physical and Chemical Research Wako-shi, Saitama 351, Japan

Received February 4, 1985

We wish to report on a novel compound unexpectedly obtained from the reaction of α-aminomalonate (AM^{2-}) with *trans*-$[CoCl_2(2,3,2\text{-tet}^3)]ClO_4$.

In our laboratory, asymmetric decarboxylations of α-amino-α-alkylmalonates (ARM^{2-}) using a chiral cobalt(III) complex containing an optical active tetraamine have been investigated.[4] Every X-ray study of some stereospecifically obtained α-amino-α-methylmalonato (AMM) complexes containing optical active tetraamines revealed[5] that the AMM ion coordinates to the central metal through the amino group and through one of the carboxyl groups in the cis-β_2 fashion, and the uncoordinated carboxyl group forms the intramolecular hydrogen bond to one of the secondary nitrogens of the tetraamine. As a continuation of our research on the series of the ARM complexes, we have recently used AM, which has an active proton in place of the alkyl group, and have tried to prepare its cobalt(III) complex with 2,3,2-tet.[6]

Contrary to our expectation from the AMM complexes, a novel compound containing a geminal diamine linkage as a result of an unexpected bond formation between the α-carbon of the AM moiety and one of the secondary nitrogens of the tetraamine was obtained and characterized by X-ray crystallography.

The complex was prepared by the same procedure as has been employed in the preparation of the ARM complexes; *trans*-$[CoCl_2(2,3,2\text{-tet})]ClO_4$ and ammonium α-aminomalonate were refluxed for 3 h in absolute methanol in the presence of triethylamine. After the solvent had been removed, the residue was dissolved in water and subjected to SP-Sephadex C-25 column chromatography. Elution with 0.01 N $NaClO_4$ produced an orange band, which is supposed to be singly charged, as the major product and a large amount of brownish species which strongly adsorbed to the resin. Concentration of the eluate yielded good orange crystals.[7]

The molecular structure of the complex established by the X-ray study[8] is illustrated in Figure 1. The tetraamine moiety coor-

(1) The University of Tokyo.

(2) The Institute of Physical and Chemical Research.

(3) The fully systematic name is 3,7-diaza-1,9-diaminononane.

(4) Ajioka, M.; Yano, S.; Matsuda, K.; Yoshikawa, S. *J. Am. Chem. Soc.* **1981**, *103*, 2459–2460.

(5) (a) Glusker, J. P.; Carrell, H. L.; Job, R.; Bruice, T. C. *J. Am. Chem. Soc.* **1974**, *96*, 5741–5751. (b) Yashiro, M.; Yano, S.; Ajioka, M.; Toriumi, K.; Ito, T.; Yoshikawa, S., unpublished results.

(6) This tetraamine was chosen because this system gave good crystals suitable for an X-ray crystallographic study. A simlar product was also obtained in the system containing (4*R*,6*R*)-4,6-dimethyl-3,7-diaza-1,9-diaminononane (5*R*,7*R*-Me_2-2,3,2-tet).

(7) Anal. ($C_{10}H_{21}N_5O_4Co{\cdot}ClO_4$) C, H, N, Cl. ^1H NMR (D_2O) 1.95–2.35, 2.50–3.35 (complicated pattern, CH_2 of 2,3,2-tet) ppm; ^{13}C NMR (D_2O) 24.6, 44.8, 45.2, 47.1, 48.8, 51.2, and 57.4 (t, CH_2 of 2,3,2-tet), 85.6 (s, α-C of AM), 176.2 and 177.1 (s, COO^- of AM) ppm; AB (H_2O) $\tilde{\nu}_{max}$ 20 700 (log ε = 2.16), 28 200 (log ε = 2.06) cm^{-1}.

0002-7863/85/1507-4351$01.50/0