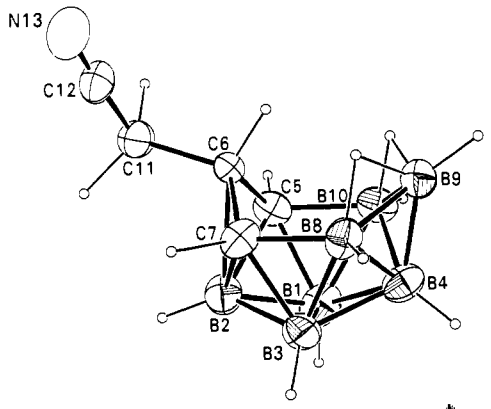

Figure 1. ORTEP drawing of the molecular structure of *arachno*-6-($NCCH_2$)-5,6,7-$C_3B_7H_{12}$. Selected bond lengths (Å) and angles (deg): C5–C6, 1.552 (6); C7–B8, 1.620 (6); B3–B8, 1.821 (8); C5–B1, 1.699 (7); B4–B8, 1.810 (8); C5–B2, 1.710 (8); B4–B9, 1.699 (9); C5–B10, 1.644 (7); B4–B10, 1.832 (8); B8–B9, 1.803 (8); C6–C7, 1.549 (6); B1–B2, 1.640 (9); B1–B3, 1.677 (9); B8–H89, 1.183 (40); C6–B2, 2.015 (8); B1–B4, 1.770 (8); B9–B10, 1.821 (8); B1–B10, 1.804 (9); C7–B2, 1.750 (7); B2–B3, 1.667 (8), C7–B3, 1.742 (7); B3–B4, 1.742 (9); C5–C6–C7, 100.9 (3); B8–B9–B10, 101.4 (4); C6–C7–B8, 110.1 (4); C6–C5–B10, 110.5 (4); C7–B8–B9, 115.1 (4); C5–B10–B9, 113.3 (4).

the puckered six-membered open face, with the C6 carbon having both *exo*-CH_2CN and *endo*-H substituents. Bridging hydrogen atoms are also present at the B8–B9 and B9–B10 edges.

Although the gross cage geometry is consistent with skeletal-electron counting predictions, examination of the interatomic cage distances reveals features that may be attributed to a hybrid "classical"/"nonclassical" nature of the cluster. The C6–C5 (1.552 (6) Å) and C6–C7 (1.549 (6) Å) distances are in the range expected for carbon–carbon single bonds. Furthermore, the C6–B2 distance is quite long (2.015 (8) Å) and the B2–B1, B2–B3, and B1–B3 distances are unusually short (~1.64–1.68 Å), when compared to similar distances in the isoelectronic analogues above or to those in *nido*-$B_{10}H_{14}$.[14] These distances suggest a reduced bonding interaction between C6 and B2 and largely localized two-center single bonds between the C6 carbon and C5 and C7. Thus, the cluster could be considered to be composed of both "classical" electron-precise and "nonclassical" electron-deficient components. In the limit where C6 and B2 are nonbonding, then instead of being considered part of the cluster framework, C6 might be viewed as a carbon–carbon bridging exopolyhedral substituent on the starting carborane framework, i.e., *arachno*-(μ-RCH)$C_2B_7H_{11}$. We have previously discussed,[1b,15] similar structural features and alternative bonding descriptions for the related hybrid nine-vertex compounds *hypho*-1-CH_2-2,5-$S_2B_6H_8$ and *hypho*-1-BH_2-2,5-$S_2B_6H_9$.

Reactions between neutral polyhedral boranes and alkynes are thought to proceed by initial electrophilic attack of the borane at the alkyne π-electron density and generally result in two-carbon insertions.[16] Clearly, the reaction reported herein involves a different reaction pathway and, accordingly, results in monocarbon rather than dicarbon insertion. The observed adjacent-carbon structure of *arachno*-6-($NCCH_2$)-5,6,7-$C_3B_7H_{12}$ is consistent with the reaction sequence shown in Figure 2 involving an initial nucleophilic attack of the *arachno*-6,8-$C_2B_7H_{12}^-$ at the γ-carbon atom of the cyanoacetylene, followed by monocarbon insertion and acetylene reduction in the manner shown to produce the tricarbon carborane with a CH_2CN substituent at C6. Additional support for this sequence comes from ^{11}B NMR spectra taken immediately after the cyanoacetylene addition, but before acidification, which show the formation of a new species exhibiting seven different

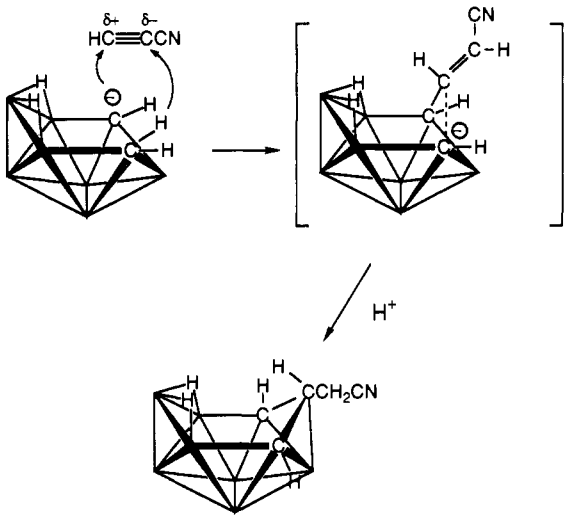

Figure 2. Possible reaction sequence leading to the formation of *arachno*-6-($NCCH_2$)-5,6,7-$C_3B_7H_{12}$.

doublet resonances[17] consistent with the structure of the asymmetric intermediate indicated in the figure. We are presently using isotopic labeling studies to determine the details of this reaction, as well as investigating the extensions of this new carbon-insertion reaction to other polyhedral borane anions.

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Supplementary Material Available: Tables of positional parameters, anisotropic temperature factors, bond distances, bond angles, and least-squares planes for *arachno*-6-($NCCH_2$)-5,6,7-$C_3B_7H_{12}$ (10 pages); listing of observed and calculated structure factors for *arachno*-6-($NCCH_2$)-5,6,7-$C_3B_7H_{12}$ (4 pages). Ordering information is given on any current masthead page.

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Identification of the Imino–Oxo Form of 1-Methylcytosine

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Interest in the tautomerism of nucleic acid bases[1] was stimulated by the suggestion by Watson and Crick[2] that this effect may be responsible for spontaneous point mutations. It has been agreed that the bases display predominantly amino-oxo tautomeric forms

† Jackson State University.
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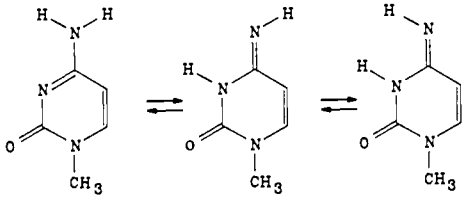
Scheme I



1 2a E 2b Z

and therefore are suitable stable "letters" of a genetic code.[3] This conclusion has been weakened by the discovery that the rare amino–hydroxy (a–h) form of 9-methylguanine occurs in *equal abundance* with the amino–oxo (a–o) form in the gas phase and in low-temperature matrices.[4] We now find that the nucleoside analogue 1-methylcytosine (1MC) also exists in these hydrophobic environments in the rare imino–oxo (i–o) form. The i–o form has also been identified (at about 10%) for *unsubstituted* cytosine,[5,6] 3-methylcytosine, and 1-methylisocytosine.[7] In earlier studies of the IR spectrum of matrix-isolated 1-methylcytosine, some weak bands were observed that could be not assigned to the a–o tautomer.[8,9]

A matrix deposit[10] of argon and 1MC (purchased from Sigma) at a ratio of about 1000:1 was irradiated with UV light from a 150-W Xe lamp passed through a 7-cm-long water filter and a WG320 cutoff filter to elminate all radiation with $\lambda < 300$ nm. No changes occur in the intense IR bands of 1MC, but the relative intensities of several weak bands present in the IR spectrum do change after about 30 min of irradiation. This effect allows us to identify a set of bands associated with a species different from the a–o tautomer of 1MC, probably a different tautomeric form of 1MC. The possibility that those new bands may arise from impurities has been carefully considered, but is rejected on the bases of gas chromatographic and mass spectrometric tests of the sample.

Using the GAUSSIAN 90 program,[11] we optimized geometries to obtain energies and IR spectra at the HF/6-31G*//HF/6-31G* level for the a–o form (**1**) and for two i–o forms of 1MC with the imino proton in the positions shown in **2a** and **2b** (Scheme I). The

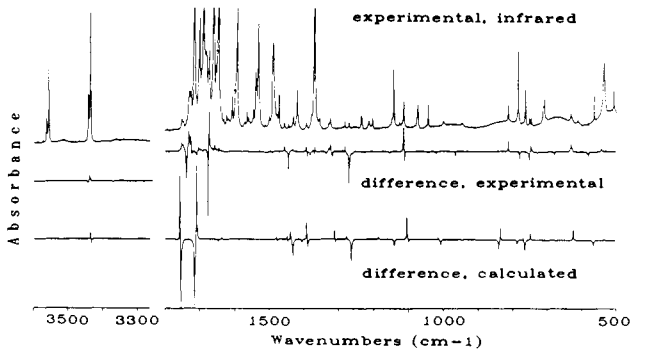


Figure 1. The upper curve shows the experimental IR spectrum of matrix-isolated 1-methylcytosine after deposition and before UV irradiation. The middle curve presents the difference between this experimental spectrum of 1MC before UV irradiation and the spectrum after irradiation. The lower curve presents the difference between the calculated IR spectrum of form **2a** of 1MC and the calculated spectrum of form **2b** of 1MC. The spectra were measured with a Nicolet Model 740 FTIR spectrometer at a spectral resolution of 1 cm^{-1}. All calculated frequencies were scaled by a single factor of 0.89.

calculated internal energy differences for the tautomers are $\Delta E°_0$(**2a**–**1**) = 4.2 kJ/mol and $\Delta E°_0$(**2b**–**1**) = 11.6 kJ/mol. If these calculated energy differences are correct,[12] the relative abundance of the i–o form is estimated to be about 10% of the a–o form and adsorption from the i–o form is expected to be observable in the IR spectra of isolated 1MC.

Figure 1 (upper curve) shows the infrared spectrum of matrix-isolated 1MC after deposition. The middle curve is the difference between the experimental IR spectrum measured before UV irradiation and that after UV irradiation. The lower curve is the difference between the calculated spectrum of form **2a** and the calculated spectrum of form **2b**. The concentration of the a–o form is not affected by UV irradiation, and IR bands from that form disappear in the experimental difference spectrum after subtraction (note the total disappearance of the characteristic bands of the amino group in the region 3400–3600 cm^{-1} and strong bands in the region 1500–1650 cm^{-1}). The positive bands in the middle experimental difference spectrum are believed to be from the imino form **2a**, which exists in the matrix deposit before irradiation, and the negative bands are from its "rotational" isomer form **2b**, which increases after irradiation. For example, a pair of bands, one negative and one positive, at about 3430 cm^{-1} is due to the N3H stretching vibrations and another, stronger pair at about 1720 cm^{-1} in the difference spectrum is due to the stretching vibrations of the carbonyl group in the two different imino forms. Spontaneous relaxation from form **2b** back to **2a** is not observed (because of a high barrier caused by the C=N double bond of the imino group), but if the irradiated matrix is now irradiated again with UV light passing through a WG280 filter instead of the WG320 filter, about 15% of form **2b** is converted back to form **2a**. When the filter is changed again to WG320, the concentration ratio reverts back almost to the situation after the first irradiation. The effect of irradiation-induced rotation about the *single* bonds has been widely observed for small groups in matrix-isolation spectroscopy,[13] but we are not aware of any studies for "rotation" about double bonds.

From the ratio of integrated intensities of the experimental absorption bands in the spectrum after initial deposition and the calculated integrated molar absorption coefficients, we estimate concentration ratios: [**2a**]/[**1**] = 0.15 ± 0.05 and [**2b**]/[**1**] = 0.03 ± 0.01. We assume that the ratios correspond to equilibria achieved in the gas phase at the temperature of the furnace (463 K) from which the sample is sublimed just before it is trapped

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in the matrix.[14] From these values of K, the standard free energy difference at 463 K can be obtained:[15] $\Delta G°_{463}(\mathbf{2a/1}) = -RT \ln K_{463}(\mathbf{2a/1}) = 7 \pm 2.5$ kJ/mol and $\Delta G°_{463}(\mathbf{2b/1}) = 13 \pm 4$ kJ/mol.

The agreement between experimental and theoretical relative energies of tautomers, together with the striking similarity between the experimental and theoretical spectra, provides strong evidence for the presence of the imino-oxo form of 1MC in the weakly interacting hydrophobic environment of the argon matrix and in the gas phase.

Acknowledgment. We thank Dr. Leszek Lapinski for directing our attention again to weak bands in the IR spectra of some cytosines and Dr. David Powell for assistance with analysis, and we are especially grateful to Dr. Krystyna Szczepaniak for critical discussions. Partial support by NIH Research Grant No. 32988 and from the Army High Performance Computing Research Center (Minneapolis, MN) and the Mississippi Center for Supercomputing Research (University, MS) is gratefully acknowledged.

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The Gas-Phase and Solution-Phase Free Energy Surfaces for $CO_2 + OH^- \rightarrow HCO_3^-$

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The reaction of CO_2 with OH^- has an important biological role in the pH regulation of blood and the transportation of CO_2 in living systems.[1] Experiments show that the forward reaction (eq 1) in water encounters an activation barrier of 13.25 kcal/mol,[2]

$$CO_2 + OH^- \rightarrow HCO_3^- \qquad (1)$$

which leads to a reaction rate too slow to be physiologically useful.[1] However, nature provides an enzyme, carbonic anhydrase (CA), to speed up the reaction by 7 orders of magnitude, which makes this enzyme reaction one of the fastest known.[3] Thus, the origin of the aqueous-phase activation barrier is a key issue in furthering our understanding of the catalytic action of CA.[3] Previous theoretical studies of this reaction in the gas phase showed no activation barrier, which led to speculation that the solution-phase barrier is induced solely by solvation effects.[4,5] A study based on a continuum solvation model did show qualitatively a solvation-induced activation barrier.[6] However, this issue still remains open for three reasons: (1) the basis sets used in the previous ab initio studies are relatively small for such a charged system; (2) the effect of finite temperature was not included;[4,5] and (3) solvation effects were not considered explicitly.[6] In this note we have addressed all of these issues and have used this information to better understand catalysis by CA.

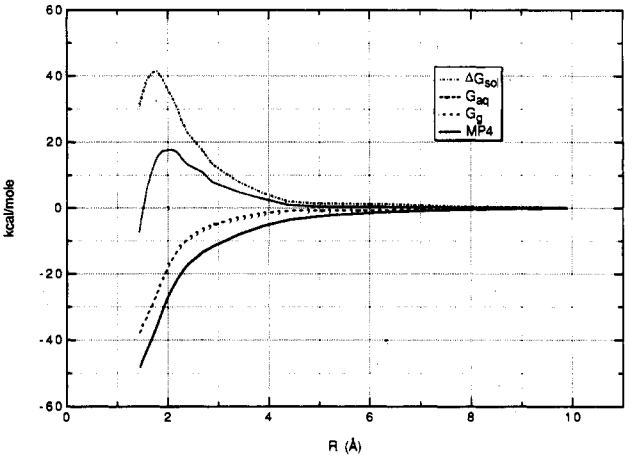

Figure 1. Calculated total energy profile (solid line, MP4), gas-phase free energy profile (dashed line, G_g), solution-phase free energy profile (dotted line, G_{aq}), and the solution-phase potential of mean force (dash-dot line, ΔG_{sol}) for $CO_2 + OH^-$.

Briefly, the ab initio gas-phase results were obtained as follows: geometries used in subsequent simulations, electrostatic potential (ESP) derived atomic point charges,[7] and thermodynamic corrections (at 298.15 K) obtained from normal mode analysis[8] were all determined at the RHF/6-31+G**//RHF/6-31+G** level. The reaction coordinate[9] was identified as the distance between the C atom of CO_2 and the O atom of OH^-,[4,5] This coordinate was fixed, and all other variables were optimized. The normal mode analysis was performed for all internal coordinates except for the reaction coordinate.[9-11] Final refinement of the total energy profile was accomplished at the MP4/6-311++G**//RHF/6-311++G** level.

We chose the zero-point reference of all thermodynamic state functions to be the separated $CO_2 + OH^-$ state. The gas-phase energy (E) and free energy (G_g) profiles are activationless (see Figure 1). This confirms the conclusion from previous studies.[4,5] The minimum energy structure for HCO_3^- is located at $R = 1.45$ Å with an E of −48.1 kcal/mol. The H and TS corrections are 1.2 and −8.7 kcal/mol, respectively. In conjunction with experimental solvation data,[12] these results enabled us to estimate the changes in thermodynamic functions for eq 1 in both the gas and aqueous phases.[13]

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(13) The thermodynamic functions (see eq 1) in the gas phase are estimated to be $\Delta G_g = -38.2 \pm 0.7$ kcal/mol, $\Delta H_g = -46.9$ kcal/mol (−49 kcal/mol as estimated by Liang and Lipscomb[5]), and $\Delta S_g = -29.2$ cal/(mol K). The corresponding values in the aqueous phase are $\Delta G_{aq} = -7.05$ kcal/mol, $\Delta H_{aq} = -10.2$ kcal/mol, and $\Delta S_{aq} = -10.9$ cal/(mol K).

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