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# Ab Initio Quantum Chemical Studies of Reactions in Astrophysical Ices 3. Reactions of $HOCH_2NH_2$ Formed in $H_2CO/NH_3/H_2O$ Ices

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Prior experimental and theoretical studies have demonstrated that reactions involving $H_2CO$ and $NH_3$ can occur in water ice mixtures even at temperatures below 100 K. The key reaction between $H_2CO$ and $NH_3$ generates monohydroxymethylamine, $HOCH_2NH_2$. The present study examines further reactions between this product and $H_2CO$ in ices. Quantum chemical calculations at the MP2/6-31+G** level indicate that while $H_2CO$ may add across the OH bond in $HOCH_2NH_2$ to yield the amine-terminated polyoxymethylene species $HOCH_2OCH_2NH_2$, it is much more favorable to add across one of the two remaining NH bonds of the original ammonia molecule to yield $(HOCH_2)_2NH$. In fact, another $H_2CO$ may add across the final NH to form the tertiary amine $(HOCH_2)_3N$. On the basis of the favorable energetics of these reactions, it is suggested that one or both of these products may be an intermediate in the pathway to the formation of hexamethylenetetramine ($C_6H_{12}N_4$), which is produced when ices containing methanol, ammonia, and water are subjected to UV irradiation and heated to room temperature.

## I. Introduction

Interstellar clouds function as vast chemical reactors that generate a wide variety of molecular species via reactions in both the gas and condensed phases and at the heterogeneous gas−grain interface. While the time frame (hundreds of thousands of years) and the ambient conditions (temperatures near 0 K and very low densities) are far beyond normal human experience with chemistry, a combination of experimental and theoretical studies can provide insight into the types of processes that function under such extremes.

One reason to pursue such investigations is to better understand the materials that might have been available during the primordial evolution of Earth's biosphere, when prebiotic chemistry began to form the building blocks of life billions of years ago. The study of reactions that can occur in astrophysical ices has become an important focus in this regard during the past decade or so. Below a certain temperature, icy mantles may form on refractory dust particles. These may subsequently accrete into larger bodies up to the size of comets, which are thought to contain largely unprocessed material from the presolar nebula from which our solar system evolved. The cometary hypothesis[1,2] suggests that infalling comets and other debris provided essential feedstock for the evolution of life on Earth, as well as some of the water in Earth's oceans. There is evidence for amino acids such as glycine in the interstellar medium (ISM),[3] and carbonaceous chondrites continue to deliver various amino acids and other organic material to Earth in the present era.[4]

Experimental studies attempt to replicate the characteristics of interstellar ices that have been studied spectroscopically by the Infrared Space Observer (ISO) or with ground-based telescopes. The goal is to match spectral features and intensities associated with molecular vibrations and thus infer the composition and processing history of extraterrestrial ices observed through either emission or absorption. Processing is a very important component of these studies given that astrophysical materials are subjected to thermal shocks, photolysis by UV and harder radiation, and radiolysis by high-energy ions. All of these conditions can be reproduced in the laboratory. In fact, due to the attenuation of the ISM, a sample can be subjected to the same amount of exposure that its interstellar counterpart would experience during a $10^6$−$10^8$ year cloud lifetime in just minutes or hours in the lab.

In photolysis experiments the sample mixture is deposited upon a cold substrate: 10−15 K for simulating interstellar cloud chemistry. It is then irradiated with UV light of suitable wavelength and subsequently heated to room temperature. IR spectra are taken at various temperature intervals to monitor the chemical alteration of the material and the sublimation or evaporation of various reactant and product species. Photolysis breaks bonds and initiates complex chemistry in ices containing significant interstellar molecules such as methanol, ammonia, carbon dioxide, and water.[5−7] Photolysis[6] of the four-component ice $H_2O/CH_3OH/CO/NH_3 = 100{:}50{:}10{:}10$ produces $CO_2$, $CH_3$, $CH_4$, $H_2CO$, HCO, $CH_3CH_2OH$, $HCONH_2$, and $CH_2CONH_2$, and RCN nitriles. One of the dominant products[6] found in the residue of these photolyzed ices that persists at room temperature is hexamethylenetetramine (HMT, $C_6H_{10}N_4$), which has a tetrahedral cage structure (Figure 1). HMT is also formed in warmer ice or slush mixtures of $H_2CO$, $NH_3$, and $H_2O$ down to at least 218 K, with no irradiation.[8]

An intriguing behavior was observed in laboratory studies that were performed at NASA-Ames Research Center in the early 1990s.[9,10] Before doing an ice photolysis experiment, a baseline run is carried out in which the sample mixture is not irradiated. The IR spectrum is expected to consist of the characteristic vibrational features of the molecular constituents of the mixture, shifted to reflect the intermolecular interactions present in the condensed phase. As the temperature is increased via slow resistive heating of the sample from ~10 K to room temperature, the components sublimate at their characteristic temperatures. The Ames group observed that certain molecular ices exhibited new and persistent spectral features that were

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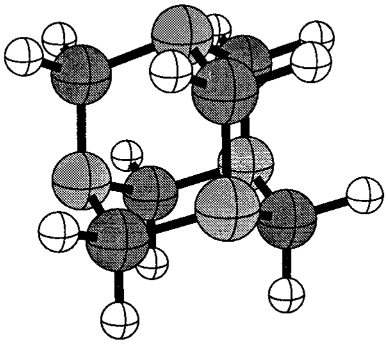

**Figure 1.** MP2/6-31G* structure of hexamethylenetetramine (HMT). Carbon and nitrogen atoms are darkly and lightly shaded, respectively ($r_{CN}$ = 1.472 Å, and $r_{CH}$ = 1.096 Å).

indicative of chemical change, despite the absence of a source of energy beyond simple heating. These ices contained formaldehyde and at least a trace of ammonia, and the reactions were found to begin at approximately 70 K. The IR spectral features of the product partially matched those of polyoxymethylene [POM, formula $(-CH_2O-)_n$] formed at room temperature from formaldehyde under acidic conditions. It was also evident that the critical polymerization process involving $H_2CO$ and $NH_3$ could initiate other reactions leading to additional products. For example, no chemistry occurred in ices containing only $H_2CO$ and $H_2O$, but when $NH_3$ was also present there was also a product thought to be due to $H_2CO-H_2O$ reactions. This suggested that a very favorable *key reaction* releases energy that may also drive *collateral reactions.* Incidentally, no HMT was produced in the experiments with no UV irradiation.

A subsequent[11] quantum chemical study (Paper 1 in this series) identified the most likely candidate for the key reaction in $H_2CO/NH_3/H_2O$ ices to be the formation of monohydroxymethylamine, $HOCH_2NH_2$, from the direct addition of $NH_3$ to $H_2CO$, a reaction that is enhanced considerably when it occurs within an ice matrix. The reaction between $H_2CO$ and $H_2O$ to yield $CH_2(OH)_2$ is also enhanced, but not enough to occur at very cold temperatures without additional energy. The POM-like product does not appear to be the result of simple polymerization reactions between two or more $H_2CO$ molecules; rather, three-body processes such as $(H_2CO)_2-NH_3 \rightarrow HOCH_2OCH_2NH_2$ and $(H_2CO)_2-H_2O \rightarrow HOCH_2OCH_2OH$ were found to be much more favorable.

The present study follows up the previous work by investigating further chemistry involving $HOCH_2NH_2$. As described below, a second $H_2CO$ can either add across the OH bond or across one of the two remaining NH bonds, and a third $H_2CO$ can add across the final NH bond. The aim of this work was to determine how favorable these processes are using quantum chemical calculations in order to evaluate whether they are likely to occur in astrophysical ices. The results suggest that the formation of the secondary or tertiary amines may contribute to the pathway to HMT in the photolysis experiments described above. After outlining the methodology, results and discussion will follow.

## II. Computational Methodology

The ice-bound reactions described below were modeled by characterizing the basic addition processes and then including one or two explicit waters that are involved chemically in the reactions. This was followed by single-point calculations in which the optimized cluster structures were embedded within a continuum solvation field to ascertain the approximate impact of bulk ice on the reaction energetics. All calculations were performed with the Gaussian[12] package of ab initio programs. Correlation was treated with frozen-core second-order Møller–Plesset perturbation theory[13] (MP2). 6-31+G** basis sets[14,15] were employed. Diffuse basis functions are important here both for describing intermolecular character as well as for transition states (TS). MP2 second derivatives were computed analytically for most of the optimized structures in order to correct relative energies for zero-point vibrational energy (ZPE) and to verify that transition states possessed only one imaginary frequency. Self-consistent reaction field calculations were performed with the isodensity-surface polarizable continuum model[16] (IPCM). A dielectric constant of 78.5 was used for water. All energy differences are given with respect to the optimized structure of the reactant complex, the proper reference for condensed-phase reactions (in contrast to the gas phase, where the energy of the separated reactants is the proper reference).

## III. Formation of $(OHCH_2)_2NH$

The focus of the present study is to determine the fate of $HOCH_2NH_2$ formed in the general ice-bound reaction

$$H_2CO - NH_3 - (H_2O)_n \rightarrow HOCH_2NH_2 - (H_2O)_n \quad (1)$$

The initial study in this series[11] found that the barrier height for the bare reaction ($n = 0$) of 33.7 kcal/mol (34.2 kcal/mol with the ZPE correction) decreased to 9.3 kcal/mol with two explicit water molecules present. The transition states for the water-catalyzed reactions indicated that concerted H transfer occurs. When the reaction components were embedded within the IPCM field, the barrier height fell to just 0.6 kcal/mol. The proton-like character of the H's in motion contributes to the preferential stabilization of the TS. Clearly, reaction 1 is strongly enhanced when it occurs within an ice matrix (i.e., for large $n$).

One possible fate of $HOCH_2NH_2$ formed in reaction 1 is the loss of water through the decomposition to methyleneimine, $CH_2NH$:

$$HOCH_2NH_2 \rightarrow CH_2NH - H_2O \quad (2)$$

However, there is a substantial barrier to this process, as Walch et al.[17] noted recently. This process was also explored in the work that led to Paper 1.[18] While a catalytic water and IPCM solvation was found to reduce the barrier height for reaction 2, it remains substantially higher than the initial barrier to addition. Thus, it appears that $HOCH_2NH_2$ will persist and be able to undergo further chemistry.

Dihydroxymethylamine, $(HOCH_2)_2NH$, is formed when $H_2CO$ adds across one of the two NH bonds in $HOCH_2NH_2$:

$$H_2CO - HOCH_2NH_2 \rightarrow (HOCH_2)_2NH \quad (3)$$

The H transfers from the N to the O in $H_2CO$, forming a second $HOCH_2$ group that binds to the N. Calculations were also run with one and two catalytic water molecules:

$$H_2CO - HOCH_2NH_2 - H_2O \rightarrow (HOCH_2)_2NH - H_2O \quad (4)$$

$$H_2CO - HOCH_2NH_2 - (H_2O)_2 \rightarrow (HOCH_2)_2NH - (H_2O)_2 \quad (5)$$

Figure 2 depicts the various reactant, TS, and product complexes (all structures and total energies for stationary points found in this work are given in Appendix S1, which may be downloaded from http://pubs.acs.org). The relative energetics at the MP2/6-31+G** level are given in Table 1, including the effect of bulk ice for each cluster size as approximated by the IPCM method. The initial cluster barrier height of 32.4 kcal/mol (31.8

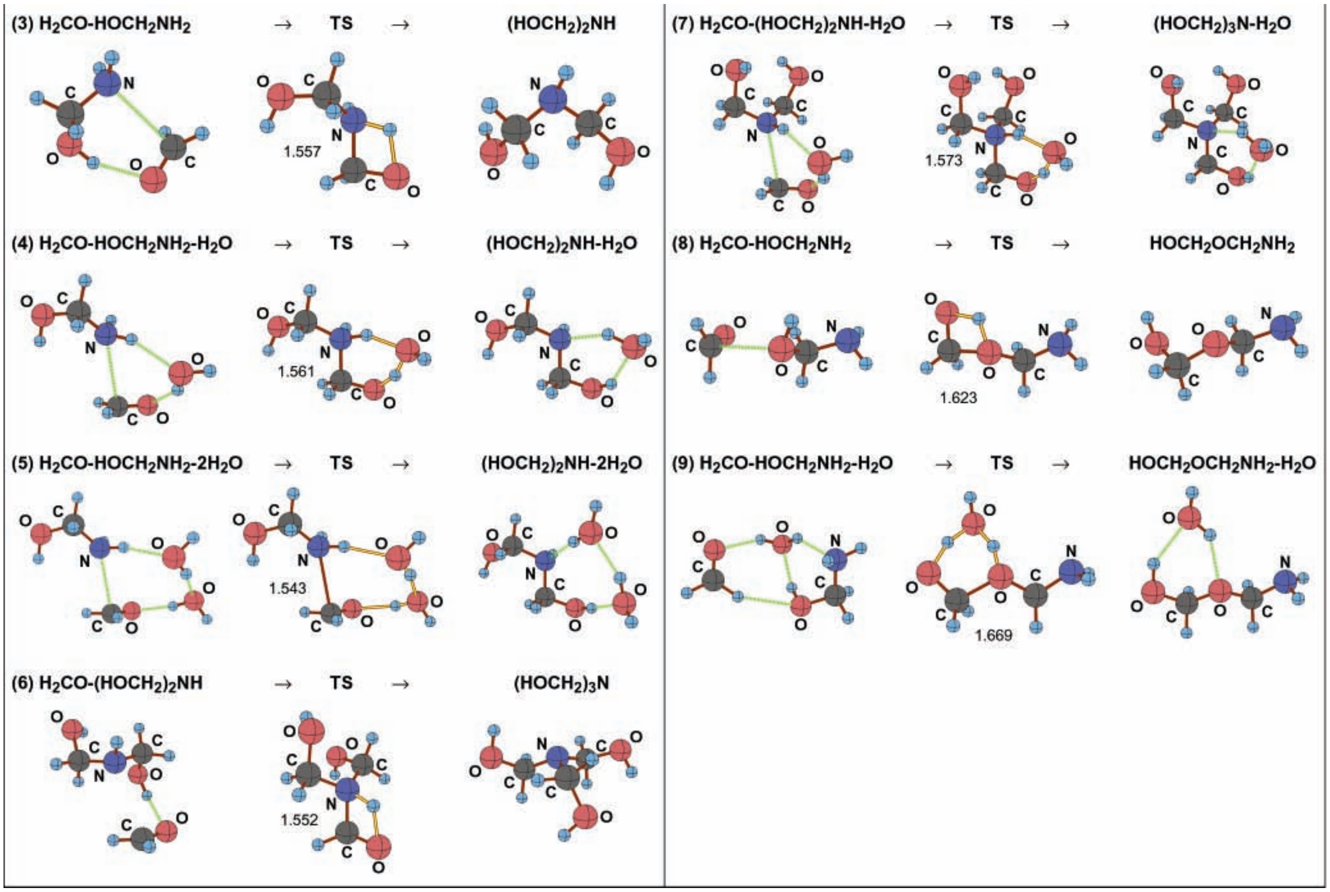

**Figure 2.** MP2/6-31+G** structures of reactant, TS, and product complexes for addition reactions between $H_2CO$ and $HOCH_2NH_2$ or $(HOCH_2)_2NH$ as described in the text. Unlabeled atoms are hydrogens. Selected bond lengths are given in Å. See Table 1 for relative energetics.

**TABLE 1: Computed Reaction Energetics[a] for Reactions between $H_2CO$ and $HOCH_2NH_2$ or $(HOCH_2)_2NH$**

| | reaction | $\Delta E_{\text{barrier}}$ cluster | $\Delta E_{\text{barrier}}$ IPCM | $\Delta E_{\text{reaction}}$ cluster | $\Delta E_{\text{reaction}}$ IPCM |
|---|---|---|---|---|---|
| (3) | $H_2CO-HOCH_2NH_2 \rightarrow (HOCH_2)_2NH$ | 32.4 (31.8) | 20.2 | −10.6 (−7.8) | −13.3 |
| (4) | $H_2CO-HOCH_2NH_2-H_2O \rightarrow (HOCH_2)_2NH-H_2O$ | 12.8 (13.2) | 4.6 | −12.6 (−9.1) | −14.1 |
| (5) | $H_2CO-HOCH_2NH_2\text{-}(H_2O)_2 \rightarrow (HOCH_2)_2NH-(H_2O)_2$ | 7.0 (7.1) | −7.8[b] | −14.1 | −22.2 |
| (6) | $H_2CO-(HOCH_2)_2NH \rightarrow (HOCH_2)_3N$ | 31.6 (30.8) | 21.9 | −8.2 (5.9) | −11.4 |
| (7) | $H_2CO-(HOCH_2)_2NH-H_2O \rightarrow (HOCH_2)_3N-H_2O$ | 15.7 (15.5) | 8.2 | −7.9 | −7.0 |
| (8) | $H_2CO-HOCH_2NH_2 \rightarrow HOCH_2OCH_2NH_2$ | 37.9 (35.6) | 33.5 | −8.5 (−5.3) | −10.8 |
| (9) | $H_2CO-HOCH_2NH_2-H_2O \rightarrow HOCH_2OCH_2NH_2-H_2O$ | 25.6 (23.8) | 22.6 | −4.8 (−2.7) | −6.3 |

[a] Energy differences in kcal/mol, with zero-point energy corrected values in parentheses; reaction numbers match text assignments. [b] TS energy lower than reactant energy (see text).

kcal/mol with ZPE correction) is very similar to the analogous value for reaction 1 (for $n = 0$). The IPCM field reduces the barrier height to 20.2 kcal/mol, a slightly larger decrease than observed in the first $H_2CO$ addition. The respective barrier heights for reactions 4 and 5 are 12.8 and 7.0 kcal/mol, which are again lower than the values of 15.0 and 9.3 kcal/mol for $n = 1$ and $n = 2$ for reaction 1. The IPCM barrier height for reaction 4 is just 4.6 kcal/mol. When the structures for reaction 5 are embedded within the IPCM field, the TS is 7.8 kcal/mol *below* the reactant complex. This may be due to a shortcoming of the IPCM method, or the optimized IPCM TS may be quite different from the cluster structure. It is also possible that the barrier is removed altogether with enough water present. In any event, the trend in energetics demonstrates that the addition of $H_2CO$ to $HOCH_2NH_2$ is at least as favorable as the initial addition of $H_2CO$ to $NH_3$.

The formation of $(HOCH_2)_2NH$ is exoergic; ice increases $\Delta E_{\text{reaction}}$, as seen in the trends both for adding active waters and for embedding reactions 3−5 in the IPCM field. The C−N bond length increases very slightly with one water, then decreases by more than 0.015 Å when the second water is added. There are several conformers of $(HOCH_2)_2NH$ that lie close to one another in energy. The most stable one also happens to be the one with the best sterics for the addition of the third $H_2CO$, as described below.

## IV. Formation of $(OHCH_2)_3N$

Trihydroxymethylamine, $(HOCH_2)_3N$, is formed when $H_2CO$ adds across the final NH bond in $(HOCH_2)_2NH$:

$$H_2CO - (HOCH_2)_2NH \rightarrow (HOCH_2)_3N \qquad (6)$$

Calculations were also run with one explicit catalytic water:

$$H_2CO - (HOCH_2)_2NH - H_2O \rightarrow (HOCH_2)_3N - H_2O \qquad (7)$$

As above, relevant structures are depicted in Figure 2 and relative energetics are given in Table 1. While the cluster barrier height for reaction 6 of 31.6 kcal/mol (30.8 kcal/mol with the ZPE correction) is lower than the values calculated for the first and second $H_2CO$ additions discussed above, the trend is reversed in the other values. The IPCM value of 21.9 kcal/mol is slightly larger than the value of 20.2 kcal/mol for reaction 3. Likewise, both the cluster and IPCM barrier heights are higher for reaction 7 than they are for reaction 4. The reaction exoergicity is also smaller for reactions 7 and 8 relative to reactions 3−5. Nevertheless, the third $H_2CO$ addition is again very clearly enhanced in an ice matrix relative to the gas-phase reaction energetics.

### V. Formation of $HOCH_2OCH_2NH_2$

While the results described above demonstrate that the addition of one, two, or even three $H_2CO$ molecules across the NH bonds of a single original ammonia molecule is very much enhanced when it occurs within an ice matrix, there are other ways in which $H_2CO$ can add to $HOCH_2NH_2$. The most likely alternative to adding across an NH bond is addition across the terminal OH:

$$H_2CO - HOCH_2NH_2 \rightarrow HOCH_2OCH_2NH_2 \tag{8}$$

As above, this process can also be catalyzed by water:

$$H_2CO - HOCH_2NH_2 - H_2O \rightarrow HOCH_2OCH_2NH_2 \text{ - } H_2O \tag{9}$$

The cluster barrier height for reaction 8 of 37.9 kcal/mol is slightly larger than the 32.4 kcal/mol barrier for addition across the NH bond with no catalytic water. As indicated by the small decrease to 33.5 kcal/mol, there is much less enhancement evident when the reaction is embedded within the IPCM field. Also, one catalytic water only reduces the cluster barrier height to 25.6 kcal/mol, and the associated IPCM value of 22.6 kcal/mol indicates that bulk ice is unlikely to provide very much more enhancement. This addition is therefore less likely than addition across the NH bond.

There is some enhancement, however, and a second and third catalytic water could bring the energetics down to the point where forming $HOCH_2OCH_2NH_2$ in this manner could at least be a collateral reaction. But this is not the most favorable pathway to the formation of this short polyoxymethylene species. As described in Paper 1, the termolecular ice-bound reaction

$$(H_2CO)_2 - NH_3 - (H_2O)_n \rightarrow HOCH_2OCH_2NH_2 - (H_2O)_n \tag{10}$$

forms $HOCH_2OCH_2NH_2$ in a single step. It is actually nearly as favorable energetically as reaction 1 and is therefore the preferred pathway to the amine-terminated POM species. It does depend on the concentrations of $H_2CO$ and $NH_3$ being large enough that there are a significant number of three-body groupings present. The multistep process described above may be the dominant pathway to $HOCH_2OCH_2NH_2$ (and longer chains as well) for lower concentrations.

### VI. Discussion and Conclusions

The quantum chemical calculations in this work and paper 1 demonstrate that the addition of $H_2CO$ to $NH_3$, $HOCH_2NH_2$, or $(HOCH_2)_2NH$ is significantly enhanced when the process occurs within an ice matrix, even at very cold temperatures. Substantial gas-phase activation barriers are mitigated to the extent that reactions can occur below 100 K, as initially observed in experimental studies.[9,10] If a mixture of $H_2CO$, $NH_3$, and $H_2O$ is heated from ~10 K to room temperature without UV irradiation, the product resembles polyoxymethylene or a derivative of POM. However, when related ice mixtures are photolyzed and then heated, very different products are observed, with hexametheylenetetramine being a dominant one. The ease with which $H_2CO$ can attack NH bonds in these ices suggests a pathway to HMT that involves $(HOCH_2)_2NH$ or $(HOCH_2)_3N$. Photolysis could remove a terminal OH group or break NH bonds. Reaction energy from radical recombination of these photolyzed species could lead to ring closure by elimination of $H_2O$, yielding more stable precursors of HMT.

Regardless of the details of these or related processes, it is intriguing that so much chemistry can occur in very cold ices composed of very simple molecules that are known to be present in the interstellar medium. The richness of the organic chemistry that can occur under the very hostile conditions of interstellar space makes it less difficult to imagine that the delivery of cometary ices to the primordial earth could have contributed to the prebiotic chemistry that led to the origin of life.

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**Supporting Information Available:** Optimized structures of all reactant, TS, and product complexes from this work, as well as their total energies and ZPE corrections. This material is available free of charge via the Internet at http://pubs.acs.org.

### References and Notes

(1) Chyba, C. N.; Thomas, P. J.; Sagan, C. *Science* **1990**, *249*, 366−373.

(2) Pendleton, Y. J.; Cruikshank, D. P. *Sky Telescope* **1994**, *87* (3), 36−42.

(3) Snyder, L. E. *Origins of Life and Evolution of the Biosphere* **1997**, *27*, 115−133.

(4) Engel, M. H.; Macko, S. A. *Nature* **1997**, *389*, 265−268.

(5) Allamandola, L. J.; Sandford, S. A.; Valero, G. J. *Icarus* **1988**, *76*, 225−252.

(6) Bernstein, M. P.; Sandford, S. A.; Allamandola, L. J.; Chang, S.; Scharberg, M. A. *Astrophys. J.* **1995**, *454*, 327−344.

(7) Allamandola, L. J.; Bernstein, M. P.; Sandford, S. A. In *Astronomical and Biochemical Origins and the Search for Life in the Universe*; Proceedings of the 5th International Conference on Bioastronomy, IAU Colloquium No. 161; Cosmovici, C. B., Bowyer, S., Werthimer, D., Eds.; Editrice Compositori: Bologna, Italy, 1997; pp 23−47.

(8) Kargel, J. S. *Icarus* **1992**, *100*, 556−574.

(9) Schutte, W. A.; Allamandola, L. J.; Sandford, S. A. *Science* **1993**, *259*, 1143−1145.

(10) Schutte, W. A.; Allamandola, L. J.; Sandford, S. A. *Icarus* **1993**, *104*, 118−137.

(11) Woon, D. E. *Icarus* **1999**, *142*, 550−556.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennuci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, Revision A2; Gaussian, Inc.: Pittsburgh, PA, 1998.

(13) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618−622.

(14) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213−222.

(15) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294−301.

(16) Foresman, J. B.; Keith, T. A.; Wiberg, K. B.; Snoonian, J.; Frisch, M. J. *J. Phys. Chem.* **1996**, *100*, 16098−16104.

(17) Walch, S. P.; Bauschlicher, C. W., Jr.; Ricca, A.; Bakes, E. L. O. *Chem. Phys. Lett.* **2001**, *333*, 6−11.

(18) Woon, D. E. Unpublished.