

## Gas-Phase Reaction of $\text{NH}_2^+$ with Acetic Acid: Implications in Astrochemistry

Laura Largo, Víctor M. Rayón, Carmen Barrientos, Antonio Largo, and  
Pilar Redondo\*

*Departamento de Química Física, Facultad de Ciencias, Universidad de Valladolid,  
47005 Valladolid, Spain*

Received July 18, 2008

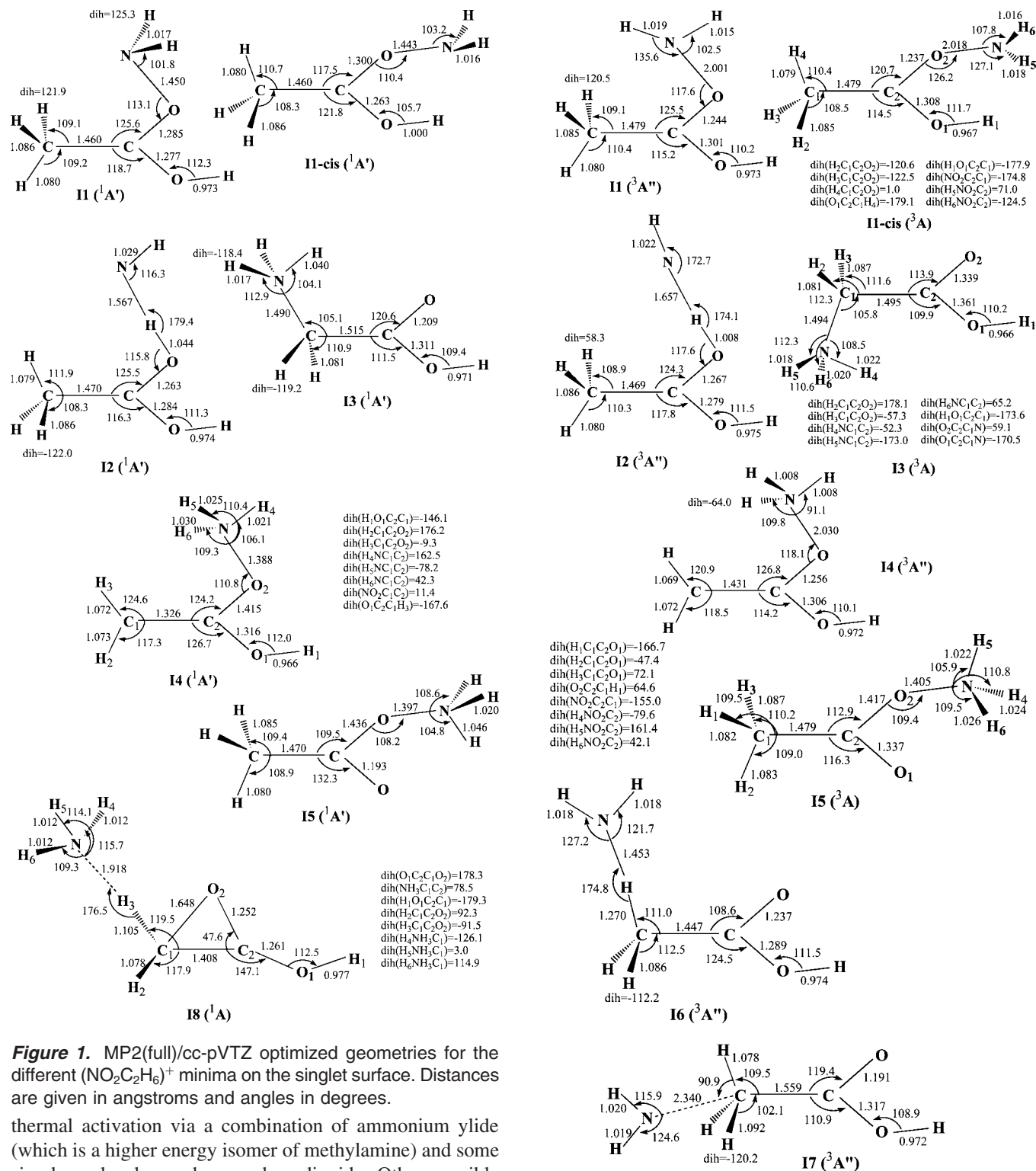
**Abstract:** A theoretical study of the ion–molecule reaction,  $\text{NH}_2^+$  with acetic acid that could lead to precursors of glycine in the interstellar medium, has been carried out on the triplet and singlet potential energy surfaces. All stationary points and transition states on the  $(\text{NO}_2\text{C}_2\text{H}_6)^+$  triplet and singlet surfaces have been determined at the MP2(full) level with the cc-pVTZ basis set. Energetic data have been obtained at the CCSD(T) level employing the aug-cc-pVTZ basis set. The global minimum of the  $(\text{NO}_2\text{C}_2\text{H}_6)^+$  system is predicted to be protonated glycine in its singlet state,  $^1\text{A}'$ , and in general singlet states are more stable than the corresponding triplet ones. Formation of ionized glycine from this reaction is shown to be a feasible process under interstellar conditions, but the proton transfer channel and the formation of the compound  $\text{CH}_2\text{COOH}^+$  seem to be more favorable processes on the triplet and singlet potential surfaces, respectively.

### Introduction

To date more than 140 molecular species have been identified in space and in interstellar clouds as well as in circumstellar envelopes. In the future this list of molecules will undoubtedly continue to grow as more powerful telescopes and interferometer arrays are built and utilized. A large fraction of these molecules is organic or carbon-based. In this way a lot of attention is devoted to the quest for biomolecules, particularly interstellar amino acids which are the basic units of proteins and therefore key elements for the origin of life. In this context, a subject that has received great interest is the origin of amino acids in the prebiotic chemistry of early Earth.<sup>1,2</sup> One of the possibilities establishes that amino acids may have first originated in the interstellar medium and were then transported to the Earth by comets and meteorites.<sup>3–7</sup> This point of view is supported by the fact that more than 70 amino acids, including eight out of 20 present in living organisms,<sup>8</sup> were isolated in the Murchison meteorite fallen in 1969. However, amino acids have not yet been detected in the interstellar medium. The simplest amino acid, glycine, has long been searched for in space, but its presence still

remains to be confirmed.<sup>9–15</sup> The difficulties in the detection of glycine can be related to the fact that glycine is a relatively large molecule, and, therefore, its rotational spectrum has relatively weak lines.<sup>16</sup> In addition, amino acids are highly susceptible to UV photodestruction,<sup>17</sup> and only in shielded environments such as dense molecular clouds and hot cores (star-forming regions) might they be detectable. However, the recent detection of amino acetonitrile,<sup>18</sup> a possible precursor of glycine, opens new possibilities of identifying more complex organic molecules in the next years. In addition, theoretical studies of the formation of amino acetonitrile in the interstellar medium have been carried out.<sup>19–21</sup> In this context, an interesting point is to determine if there are efficient synthetic routes toward amino acids, in particular toward glycine the simplest one, under interstellar conditions. According to the Miller experiment,<sup>1</sup> amino acids and in particular glycine can be synthesized by mixtures of  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{H}_2$ . Maeda and Ohno in their theoretical studies have proposed a synthetic route of glycine from simple molecules ( $\text{NH}_2$ ,  $\text{CH}_2$ , and  $\text{CO}_2$ ) in two steps;<sup>22</sup> alternatively they show that the one step reaction of aceto-lactone with ammonia can produce glycine, and its activation barrier is only 1.6 kcal/mol.<sup>23</sup> In a recent work,<sup>24</sup> they also predict that glycine and its analogs can be generated without

\* Corresponding author fax: 34-983-423013; e-mail: predondo@qf.uva.es.



**Figure 1.** MP2(full)/cc-pVTZ optimized geometries for the different (NO<sub>2</sub>C<sub>2</sub>H<sub>6</sub>)<sup>+</sup> minima on the singlet surface. Distances are given in angstroms and angles in degrees.

thermal activation via a combination of ammonium ylide (which is a higher energy isomer of methylamine) and some simple molecules such as carbon dioxide. Other possible routes of amino acids, which are very relevant in interstellar chemistry, are gas-phase ion–molecule reactions initiated by cosmic and ultraviolet radiation, since such reactions are known to be involved in the formation of many other molecules in the interstellar medium.<sup>25</sup> Recent theoretical and experimental studies<sup>26,27</sup> show that glycine and  $\beta$ -alanine could be formed in the interstellar medium by the gas-phase reactions of protonated and ionized hydroxylamine with acetic and propanoic acids. The importance of this route is not known because NH<sub>2</sub>/OH<sup>+</sup> has not yet been observed in the interstellar space. In a previous work,<sup>28</sup> we have carried

**Figure 2.** MP2(full)/cc-pVTZ optimized geometries for the different (NO<sub>2</sub>C<sub>2</sub>H<sub>6</sub>)<sup>+</sup> minima on the triplet surface. Distances are given in angstroms and angles in degrees.

out a theoretical study of various ion–molecule reactions that could lead to precursors of interstellar glycine where their reaction enthalpies have been calculated at different levels of theory. The most favorable reaction from the thermochemical viewpoint is the reaction of the cation NH<sub>2</sub><sup>+</sup> with acetic acid. This is predicted to lead to ionized glycine (NH<sub>2</sub>CH<sub>2</sub>COOH<sup>+</sup>), but charge transfer reaction was predicted

**Table 1.** Relative Energies (kcal/mol) for the Relevant  $(\text{NO}_2\text{C}_2\text{H}_6)^+$  Species in the Reaction of  $\text{NH}_2^+$  with  $\text{CH}_3\text{COOH}^a$ 

| singlet surface  |                         |                      | triplet surface  |                         |                      |
|--|-------------------------|----------------------|--|-------------------------|----------------------|
| isomer   | $\Delta E$ (MP2 = full) | $\Delta E$ (CCSD(T)) | isomer   | $\Delta E$ (MP2 = full) | $\Delta E$ (CCSD(T)) |
| $\text{CH}_3\text{COOHNH}_2^+ \text{I1}^+(\text{A}')$        | 57.43                   | 53.18                | $\text{CH}_3\text{COOHNH}_2^+ \text{I1}^+(\text{A}'')$         | 110.66                  | 101.62               |
| $\text{CH}_3\text{COOHNH}_2^+ \text{I1-cis}^+(\text{A}')$    | 51.49                   | 47.99                | $\text{CH}_3\text{COOHNH}_2^+ \text{I1-cis}^+(\text{A})$       | 113.60                  | 103.92               |
| $\text{CH}_3\text{COOHHNH}^+ \text{I2}^+(\text{A}')$         | 138.52                  | 123.67               | $\text{CH}_3\text{COOHHNH}^+ \text{I2}^+(\text{A}'')$          | 88.45                   | 80.92                |
| $\text{NH}_3\text{CH}_2\text{COOH}^+ \text{I3}^+(\text{A}')$ | 0.00                    | 0.00                 | $\text{NH}_3\text{CH}_2\text{COOH}^+ \text{I3}^+(\text{A})$    | 111.29                  | 99.93                |
| $\text{CH}_2\text{COOHNH}_3^+ \text{I4}^+(\text{A}')$        | 82.95                   | 79.37                | $\text{CH}_2\text{COOHNH}_3^+ \text{I4}^+(\text{A}'')$         | 148.32                  | 139.17               |
| $\text{CH}_3\text{COONH}_3^+ \text{I5}^+(\text{A}')$         | 47.57                   | 45.37                | $\text{CH}_3\text{COONH}_3^+ \text{I5}^+(\text{A})$            | 164.02                  | 149.74               |
|  |                         |                      | $\text{NH}_2\text{HCH}_2\text{COOH}^+ \text{I6}^+(\text{A}'')$ | 124.37                  | 122.20               |
|  |                         |                      | $\text{NH}_2\text{CH}_3\text{COOH}^+ \text{I7}^+(\text{A}'')$  | 128.65                  | 124.01               |
| $\text{NH}_3\text{HCHCOOH}^+ \text{I8}^+(\text{A})$          | 64.24                   | 63.57                |  |                         |                      |

<sup>a</sup> Zero-point vibrational energy differences have been included.**Table 2.** Relative Energies (kcal/mol) for the Possible Products of the Reaction  $\text{NH}_2^+$  with  $\text{CH}_3\text{COOH}$ , on the Triplet and Singlet Potential Energy Surfaces<sup>a</sup>

| triplet surface  | $\Delta E$ (MP2 = full) | $\Delta E$ (CCSD(T)) | singlet surface  | $\Delta E$ (MP2 = full) | $\Delta E$ (CCSD(T)) |
|--|-------------------------|----------------------|--|-------------------------|----------------------|
| $\text{NH}_2^+(\text{B}_2) + \text{CH}_3\text{COOH}(\text{A}')$        | 0.00                    | 0.00                 | $\text{NH}_2^+(\text{A}_1) + \text{CH}_3\text{COOH}(\text{A}')$        | 0.00                    | 0.00                 |
| $\text{NH}_2(\text{B}_1) + \text{CH}_3\text{COOH}^+(\text{A}')$        | -2.88                   | -11.39               | $\text{NH}_2(\text{B}_1) + \text{CH}_3\text{COOH}^+(\text{A}')$        | -39.17                  | -41.46               |
| $\text{CH}_3\text{COONH}_2^+(\text{A}'') + \text{H}(\text{S})$         | -2.97                   | 2.19                 | $\text{CH}_3\text{COONH}_2^+(\text{A}'') + \text{H}(\text{S})$         | -39.26                  | -27.88               |
| $\text{NH}_2\text{CH}_2\text{COOH}^+(\text{A}'') + \text{H}(\text{S})$ | -31.22                  | -26.93               | $\text{NH}_2\text{CH}_2\text{COOH}^+(\text{A}'') + \text{H}(\text{S})$ | -67.51                  | -57.00               |
| $\text{NH}(\text{S}) + \text{CH}_3\text{C}(\text{OH})_2^+(\text{A}')$  | -36.92                  | -39.15               | $\text{NH}(\text{A}) + \text{CH}_3\text{C}(\text{OH})_2^+(\text{A}')$  | -19.08                  | -25.51               |
| $\text{NH}_3(\text{A}_1) + \text{CH}_2\text{COOH}^+(\text{A}')$        | -62.78                  | -58.10               | $\text{NH}_3(\text{A}_1) + \text{CH}_2\text{COOH}^+(\text{A}')$        | -99.07                  | -88.17               |

<sup>a</sup> ZPV energy corrections have been included.

as a competitive process. Both reactants are present in the interstellar medium.<sup>29,30</sup> It is well-known that to play a role in the interstellar chemistry reactions in addition to being exothermic must be barrier free. However, a full exploration of the potential energy surface is required to ascertain whether energetic barriers are present. On the other hand, ion–molecule reactions of ionized amine fragment compounds with neutral carboxylic acid and ester species have been experimentally investigated in a selected ion flow tube (SIFT) at 298 K.<sup>31</sup> These studies suggest that  $\text{NH}_2^+$  reacts with acetic acid via proton transfer giving  $\text{CH}_3\text{CO}(\text{OH})_2^+ + \text{NH}$  as products (the formation of these products are not been considered in our previous theoretical study). In order to explain this experimental result in this work we have carried out a detailed theoretical study of the reaction of  $\text{NH}_2^+$  with acetic acid considering both the triplet and singlet potential energy surfaces. We will try to determine if under interstellar conditions the formation of glycine ionized is viable from this reaction and to provide a reasonable interpretation of the mass spectrometry experiments.<sup>31</sup> It should be noted that theoretical studies in this field are very appropriate because the conditions present in molecular clouds (low pressure and temperature) are almost ideal for the application of theoretical methods.

## Computational Methods

The geometries of the different species involved in the reaction of  $\text{NH}_2^+$  with acetic acid have been obtained at the second-order Moller–Plesset level including all the electrons in the calculations. In these optimizations the cc-pVTZ (correlation-consistent polarized valence triple- $\zeta$ ) basis set developed by Dunning<sup>32,33</sup> has been employed. Each optimized structure was verified to be a stationary point or a transition state by vibrational analysis carried out at the same level (MP2(full)/cc-pVTZ).

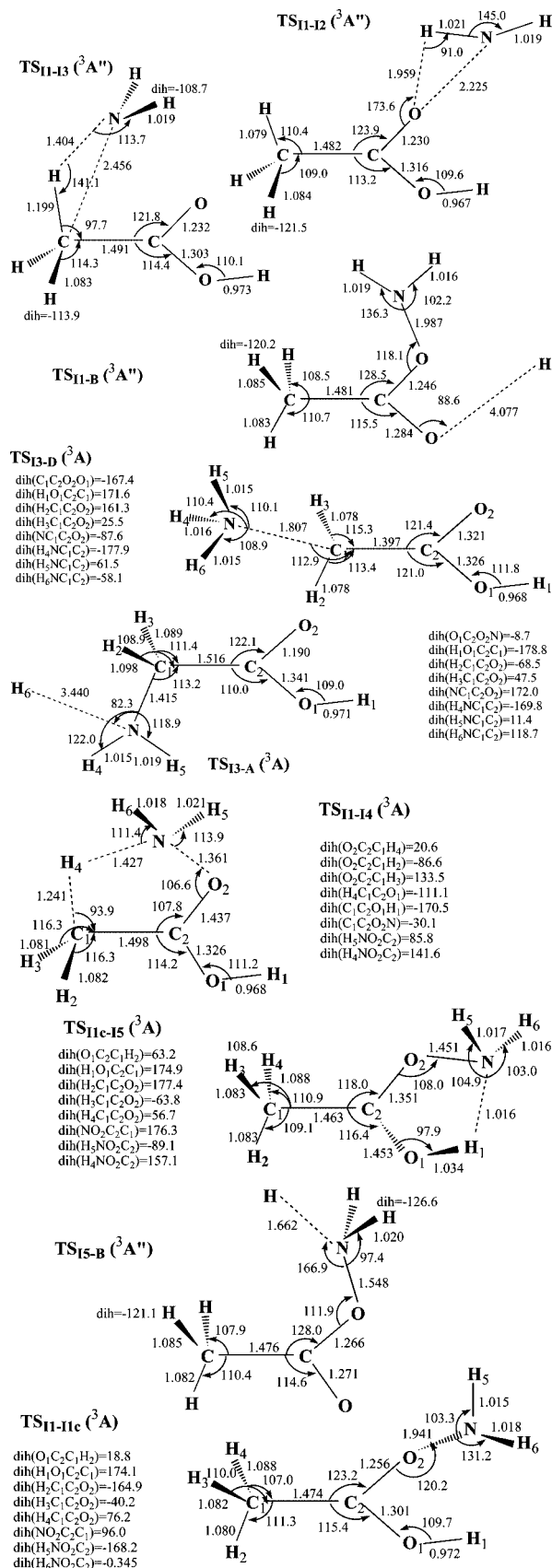
In order to compute accurate relative energies CCSD(T) calculations (coupled-cluster single and double excitation model augmented with a noniterative triple excitation correction)<sup>34</sup> have been carried out on the MP2(full)/cc-pVTZ geometries. The aug-cc-pVTZ basis set, which also includes diffuse functions, has been employed for the energetic calculations. Zero-point vibrational (ZPV) energy corrections were included at the MP2(full)/cc-pVTZ level.

All calculations reported in this work were carried out with the *Gaussian-98* program package.<sup>35</sup>

## Results and Discussion

In the present study the possible intermediate species as well as the relevant transition states of the reaction of  $\text{NH}_2^+$  with acetic acid have been characterized. Given the multiplicity of the reactants ( $\text{NH}_2^+$  ( $^3\text{B}_1$ ) and  $\text{CH}_3\text{COOH}$  ( $^1\text{A}'$ )), this reaction should take place in principle on the triplet potential energy surface. In addition to the detailed study of the triplet surface, we have also analyzed the singlet potential energy surface to check a possible implication of this surface through an intersystem-crossing process.

**1.  $(\text{NO}_2\text{C}_2\text{H}_6)^+$  Isomers.** In this section we will briefly describe the stationary points found on the  $(\text{NO}_2\text{C}_2\text{H}_6)^+$  triplet and singlet surfaces. Only the minima that are relevant in the reaction of  $\text{NH}_2^+$  with acetic acid will be reported. The optimized geometries of the singlet isomers are collected in Figure 1 and the corresponding to the triplet ones in Figure 2, whereas the relative energies of both singlet and triplet isomers are shown in Table 1. All the isomers considered in Figures 1 and 2, are tested to be true minima on their respective potential surfaces. Similar structures are implicated in both surfaces with the exception of I6 and I7, which correspond to the direct interaction of the nitrogen atom in the  $\text{NH}_2^+$  ion with a hydrogen or the carbon atom, respectively, of the  $\text{CH}_3$  group of acetic acid. Both species are true



**Figure 3.** MP2(full)/cc-pVTZ optimized geometries for the relevant transition states involved in the reaction  $NH_2^+(^3B_1)$  with  $CH_3COOH(^1A')$ . Distances are given in angstroms and angles in degrees.

minima on the triplet surface and are not located on the singlet one. On the other hand, isomer I8, corresponding to

a van der Waals complex between  $NH_3$  and  $CH_2COOH^+$ , is only located on the singlet potential surface. In both surfaces the direct interaction of  $NH_2^+$  ion through the nitrogen atom with the oxygen atom of the carboxylic group of acetic acid gives isomers I1 and I1-cis, corresponding to two relative positions of the  $NH_2$  and OH groups in the molecule. The other isomers which are involved in the reaction are obtained from these two by different isomerization processes which will be explained in the next sections.

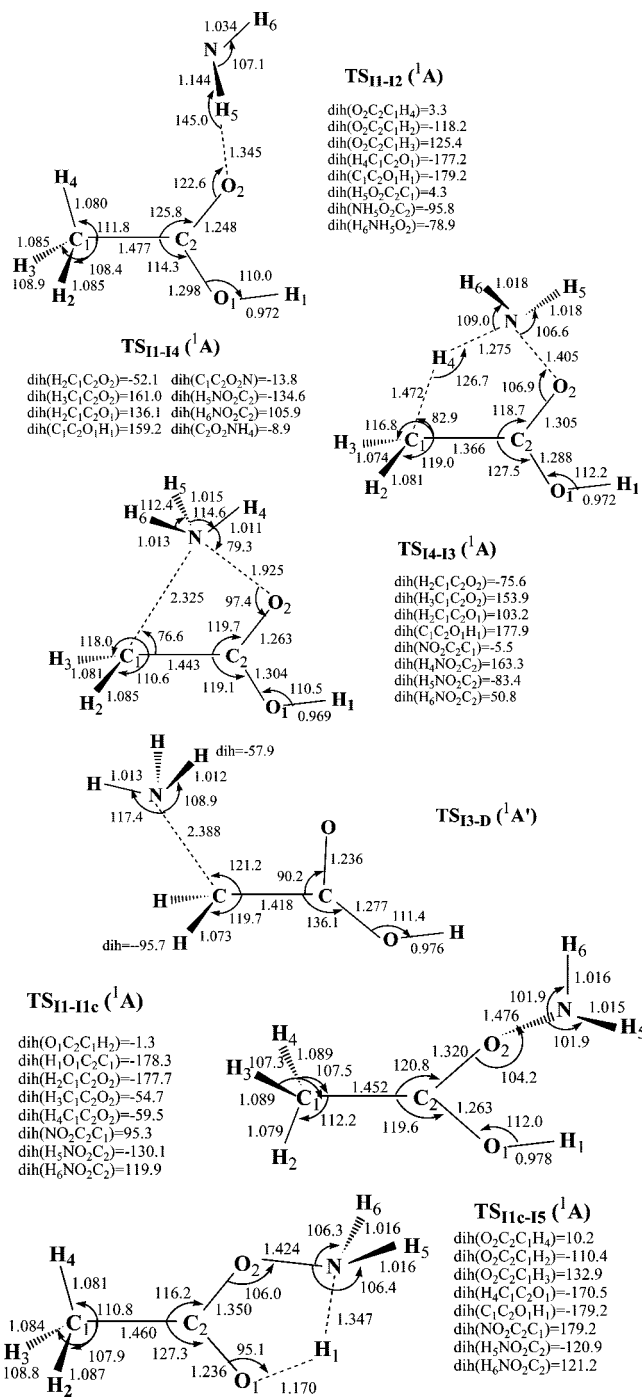
In general we can see from Figures 1 and 2 that the N–O bond distances are clearly longer for triplet than for singlet isomers. The C–C bond distance is in general similar to typical carbon–carbon single bond, with the exception of isomer I4 ( $^1A'$ ) where the C–C bond distance has a certain double character. Finally, the C–N distances are found to be similar in triplet and singlet states.

Concerning the relative stabilities of the different intermediates collected in Table 1, we can observe that the energy values calculated at both levels of theory, MP2=full and CCSD(T), give similar stability order between the species considered. Only a change is found on the relative stability of triplet isomers I3 and I1, whose energy difference is only about 1 kcal/mol. The global minimum is predicted to be isomer I3 in its singlet state,  $^1A'$ , which corresponds to protonated glycine. With the only exception of isomer I2, singlet states are more stable than the corresponding triplet ones. In a previous study of the  $(NO_2C_2H_6)^+$  singlet potential surface,<sup>36</sup> the ion derived from protonation of glycine on the amine group is also found as the lowest-lying. On the singlet potential energy surface the stability order found at both levels of theory is ( $>$  means more stable than) as follows: I3 ( $^1A'$ ) > I5 ( $^1A'$ ) > I1-cis ( $^1A'$ ) > I1 ( $^1A'$ ) > I8 ( $^1A'$ ) > I4 ( $^1A'$ ) > I2 ( $^1A'$ ). Above the protonated glycine we found isomers I5, I1, and I1-cis, which are quite close in energy (about 45–53 kcal/mol above the global minimum at the CCSD(T) level) and have one nitrogen–oxygen bond. The van der Waals complex is located above isomer I4 that also has a N–O bond. The less stable isomer is I2, which could be seen as a result of the interaction of  $NH_2^+$  ion through one hydrogen atom with the oxygen atom of the carboxylic group. If we observe the relative stabilities of the triplet isomers, we can see that the main difference is found for isomer I2, which is the most unstable on the singlet surface, whereas on the triplet one it corresponds to the most stable structure. Another significant difference is that structure I5 is found to be the most unstable one on the triplet surface. On the triplet surface protonated glycine, I3, is less stable than the global minimum, and it is located 19.01 kcal/mol above structure I2. Other common isomers have similar relative energies on both surfaces. The stability order on the triplet surface at the CCSD(T) level is the following: I2 ( $^3A''$ ) > I3 ( $^3A$ ) > I1 ( $^3A''$ ) > I1-cis ( $^3A$ ) > I6 ( $^3A''$ ) > I7 ( $^3A''$ ) > I4 ( $^3A''$ ) > I5 ( $^3A$ ).

**2. Reaction of  $NH_2^+$  with Acetic Acid.** We will discuss in this section the different pathways of the reaction of  $NH_2^+$  ion with acetic acid. One possible product of this reaction is ionized glycine; however, other possible channels could be competitive. Therefore, we should consider the following possibilities:



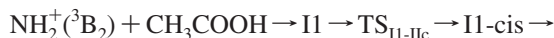
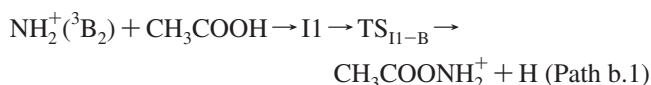




**Figure 5.** MP2(full)/cc-pVTZ optimized geometries for the relevant transition states involved in the reaction of excited  $\text{NH}_2^+(\text{}^1\text{A}_1)$  with  $\text{CH}_3\text{COOH}(\text{}^1\text{A}')$ . Distances are given in angstroms and angles in degrees.

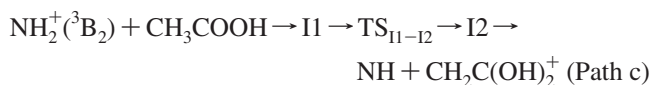
$\text{TS}_{13-\text{A}}$ , which has a relative energy quite similar to  $\text{TS}_{11-13}$ , would lead to ionized glycine.

The  $\text{CH}_3\text{COONH}_2^+$ , which is quasi-isoenergetic with the reactants, can be obtained through two different paths. One of them, path b.1, implies hydrogen atom elimination through transition state  $\text{TS}_{11-\text{B}}$ . The second path, b.2, involves two isomerization processes leading to isomers I1-cis and I5, followed by hydrogen atom elimination:

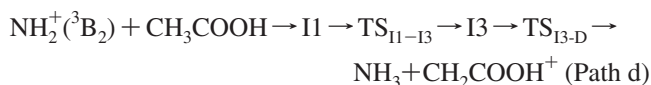


The transition states and isomer I5 involved in both paths are clearly located above the reactants. This barrier quite likely would prevent the formation of  $\text{CH}_3\text{COONH}_2^+$  in space.

Another exothermic and barrier free process is isomerization of I1 into isomer I2, through transition state  $\text{TS}_{11-12}$ , lying 24.6 kcal/mol below the reactants. The intermediate formed I2, produces  $\text{NH} + \text{CH}_3\text{C}(\text{OH})_2^+$ , through direct NH elimination and does not seem to involve any transition state. We carried out a scan for this process, performing optimizations at different N–H distances and found no sign of transition state:



The formation of  $\text{NH}_3 + \text{CH}_2\text{COOH}^+$  involves the same three phases as path a giving isomer I3. Once isomer I3 is obtained, products D are obtained through  $\text{NH}_3$  abstraction. This process involves transition state  $\text{TS}_{13-\text{D}}$ . The global process is exothermic and barrier free:

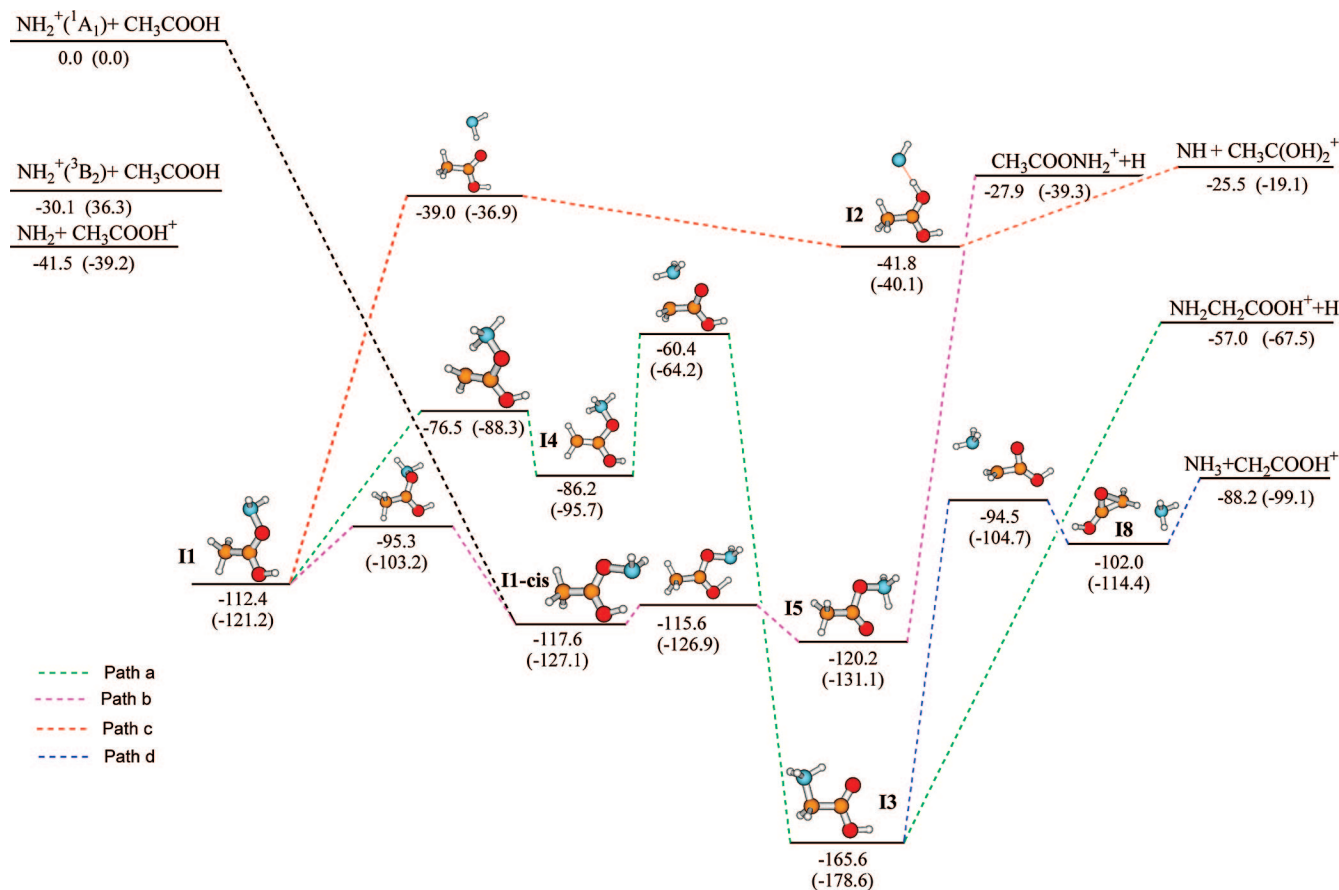


Finally, isomer I1 could give isomer I4 through hydrogen atom migration involving transition state  $\text{TS}_{11-14}$ . This process is not relevant in the context of interstellar chemistry, because it has a significant activation barrier. The transition state is clearly located above the reactants, and formation of isomer I4 is an endothermic process. Therefore, evolution of isomer I4 has not been considered.

Theoretical calculations on the triplet potential energy surface suggest that paths a, c, and d are feasible processes under interstellar conditions that preclude reaction that are endothermic or proceed through significant activation barriers. The most exothermic channel is d, production of  $\text{NH}_3 + \text{CH}_2\text{COOH}^+$ . However, the most favorable channel from kinetic arguments should be proton transfer process, which has lower activation barriers (notice that  $\text{TS}_{11-12}$  lies lower in energy than  $\text{TS}_{11-13}$ ). The less favorable one seem to be formation of ionized glycine. It should be remarked that our results agree with the results from SIFT experiments,<sup>31</sup> since production of  $\text{NH} + \text{CH}_3\text{C}(\text{OH})_2^+$  is observed.

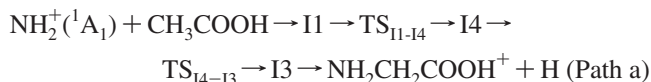
**2.1. Singlet Potential Energy Surface.** The geometries of the transition states located on the singlet surface are collected in Figure 5, and the energy profile for the reaction  $\text{NH}_2^+(\text{}^1\text{A}_1) + \text{CH}_3\text{COOH}(\text{}^1\text{A}')$  is shown in Figure 6. As in the case of the triplet potential energy surface, all transition states have been checked to have one imaginary frequency associated with the corresponding reaction coordinate.

The most favorable interaction of  $\text{NH}_2^+(\text{}^1\text{A}_1)$  ion with acetic acid occurs between nitrogen and oxygen atoms giving I1 and I1-cis as in the case of the triplet surface. However, in this case the most stable process is the



**Figure 6.** Energy profile, in kcal/mol, for the reaction of excited  $\text{NH}_2^+(^1\text{A}_1)$  with  $\text{CH}_3\text{COOH}(^1\text{A})$  at the CCSD(T) and MP2(full) (in parentheses) levels (including zero-point vibrational energy differences).

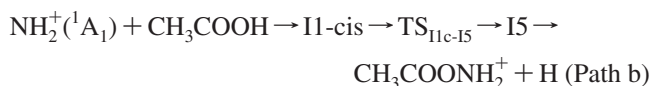
formation of isomer I1-cis. Both isomers can be reached and isomerization implies transition state  $\text{TS}_{\text{I1-I1c}}$ . From isomer I1, the process giving ionized glycine on the singlet potential energy surface has some differences with respect to that on the triplet one and proceeds through the following steps:



Isomerization of I1 into I4 implies a proton transfer from the carbon atom to the nitrogen one through transition state  $\text{TS}_{\text{I1-I4}}$ . The migration of the  $\text{NH}_3$  group from oxygen to carbon gives protonated glycine, I3, and this process implies transition state  $\text{TS}_{\text{I4-I3}}$ . The direct elimination of one of the hydrogens bonded to nitrogen gives ionized glycine. The global process giving ionized glycine is exothermic and barrier free (both transition states are located below the reactants, about  $-76.5$  and  $-60.4$  kcal/mol, respectively). Protonated glycine is a very stable intermediate and could be a long-lived species given its energy difference with the reaction products.

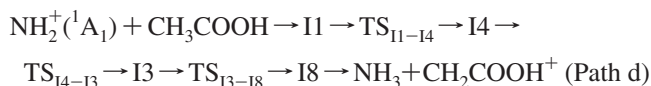
Path b, leading to  $\text{CH}_3\text{COONH}_2^+$ , shows similar steps to those found on the triplet surface for path b.2. In this case isomer I1-cis is formed directly from the reactants, and the only difference is the last step. On the singlet surface, elimination of hydrogen atom is a direct process, which does not seem to involve any transition state. On

the singlet surface the process is exothermic and barrier free. This process can be summarized as



The path for the formation of  $\text{NH} + \text{CH}_3\text{C}(\text{OH})_2^+$ , path c, has the same steps as that on the triplet surface, but in this case isomer I2 is relatively less stable and the NH is formed in an excited state ( $^1\Delta$ ).

Finally, another channel is originated from protonated glycine, I3, by fragmentation into  $\text{NH}_3 + \text{CH}_2\text{COOH}^+$ :



When  $\text{NH}_3$  is eliminated from I3 through  $\text{TS}_{\text{I3-I8}}$ , a van der Waals complex is formed before dissociation. It can be seen in Figure 6 that once I3 is formed path d seems to be more favorable than path a, from a thermodynamic point of view.

All the processes considered on the singlet potential energy surface are exothermic and barrier-free and therefore feasible under the conditions in the interstellar space. The last process, formation of  $\text{NH}_3 + \text{CH}_2\text{COOH}^+$ , seems to be in principle the most favorable one. Since in the experiments<sup>31</sup> only  $\text{NH} + \text{CH}_3\text{C}(\text{OH})_2^+$  are observed as products, it seems that the



reaction takes place only on the triplet surface, and the singlet one is not reached.

## Conclusions

A theoretical study of the reaction of  $\text{NH}_2^+$  ion with acetic acid has been carried out on the triplet and singlet potential energy surfaces. We have characterized the possible intermediate species as well as the relevant transition states for this reaction. The lowest-lying species of the  $(\text{NO}_2\text{C}_2\text{H}_6)^+$  system is found to be protonated glycine in its singlet state,  $^1\text{A}'$ . With the only exception of isomer I2, singlet states are more stable than the corresponding triplet ones. For the  $(\text{NO}_2\text{C}_2\text{H}_6)^+$  system the stability order found is the following: I3 ( $^1\text{A}'$ ) > I5 ( $^1\text{A}'$ ) > I1-cis ( $^1\text{A}'$ ) > I1 ( $^1\text{A}'$ ) > I8 ( $^1\text{A}$ ) > I4 ( $^1\text{A}'$ ) > I2 ( $^3\text{A}''$ ) > I3 ( $^3\text{A}$ ) > I1 ( $^3\text{A}''$ ) > I1-cis ( $^3\text{A}$ ) > I6 ( $^3\text{A}''$ ) > I2 ( $^1\text{A}'$ ) > I7 ( $^3\text{A}''$ ) > I4 ( $^3\text{A}''$ ) > I5 ( $^3\text{A}$ ).

Theoretical calculations on the triplet potential energy surface suggest that paths, a, c and d, giving ionized glycine, proton transfer products, and the  $\text{CH}_2\text{COOH}^+$  compound, respectively, are feasible processes under interstellar conditions. The most favorable channel, from kinetic arguments, should be the proton transfer process, which has lower activation barriers. The less favorable one seems to be formation of ionized glycine. On the other hand, all the processes considered on the singlet potential energy surface are exothermic and barrier-free and therefore feasible under the conditions in the interstellar space. The formation of  $\text{NH}_3 + \text{CH}_2\text{COOH}^+$  seems to be in principle the most favorable one. Experimental results observed from SIFT experiments<sup>31</sup> show that the products correspond to the proton transfer process ( $\text{NH} + \text{CH}_3\text{C}(\text{OH})_2^+$ ), in agreement with the theoretical results found on the triplet potential energy surface. Therefore the present theoretical study provides a reasonable interpretation of the experiments.

Our results suggest that even if the formation of ionized glycine from the reaction of  $\text{NH}_2^+$  ion with acetic is a favorable process under interstellar conditions, there are other competitive channels that are most favorable.

**Acknowledgment.** This research has been supported by the Ministerio de Educación y Ciencia of Spain (Grant CTQ2007-67234-C02-02) and by the Junta de Castilla y León (Grants VA 077A06 and VA 006B07).

**Supporting Information Available:** Optimized geometries of the reactants and products (Figures S1 and S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Miller, S. L. *Science* **1953**, *117*, 528.
- (2) De Duve, C. *Origins Life Evol. Biospheres* **2003**, *33*, 559.
- (3) Winnewisser, G.; Herbst, E. *Rep. Prog. Phys.* **1993**, *56*, 1209.
- (4) Tielens, A. G. G. M.; Charnley, S. B. *Origins Life Evol. Biospheres* **1997**, *27*, 23.
- (5) Combes, F.; Rieu, N. Q.; Wlodarczak, G. *Astron. Astrophys.* **1996**, *308*, 618.
- (6) Bernstein, M. P.; Dworkin, J. P.; Sandford, S. A.; Cooper, G. W.; Allamandola, L. J. *Nature* **2002**, *416*, 401.
- (7) Chyba, C.; Sagan, D. *Nature* **1992**, *335*, 125.
- (8) Cooper, G. W.; Onwo, W. M.; Cronin, J. R. *Geochim. Cosmochim. Acta* **1992**, *57*, 4109.
- (9) Hollis, J. M.; Snyder, L. E.; Suenram, R. D.; Lovas, F. J. *Astrophys. J.* **1980**, *241*, 1001.
- (10) Snyder, L. E.; Hollis, J. M.; Suenram, R. D.; Lovas, F. J.; Brown, L. W.; Buhl, D. *Astrophys. J.* **1983**, *268*, 123.
- (11) Ceccarelli, C.; Loinard, L.; Castets, A.; Faure, A.; Lefloch, B. *Astron. Astrophys.* **2000**, *362*, 1122.
- (12) Hollis, J. M.; Pedelty, J. A.; Boboltz, D. A.; Liu, S.-Y.; Snyder, L. E.; Palmer, P.; Lovas, F. J.; Jewell, P. R. *Astrophys. J. Lett.* **2003**, *596*, L235.
- (13) Hollis, J. M.; Pedelty, J. A.; Snyder, L. E.; Jewell, P. R.; Lovas, F. J.; Palmer, P.; Liu, S.-Y. *Astrophys. J.* **2003**, *588*, 353.
- (14) Kuan, J.-Y.; Charnley, S. B.; Huang, H.-C.; Tseng, W.-L.; Kisiel, Z. *Astrophys. J.* **2003**, *593*, 848.
- (15) Snyder, L. E.; Lovas, F. J.; Hollis, J. M.; Friedel, D. N.; Jewell, P. R.; Remijan, A.; Ilyushin, V. V.; Alekseev, E. A.; Dyubko, S. F. *Astrophys. J.* **2005**, *619*, 914.
- (16) Irvine, W. *Origins Life Evol. Biosphere* **1998**, *28*, 365.
- (17) Ehrenfreund, P.; Bernstein, M.; Dworkin, J. P.; Sandford, S. A.; Allamandola, L. *Astrophys. J.* **2001**, *550*, L95.
- (18) Belloche, A.; Menten, K. M.; Comito, C.; Müller, H. S. P.; Schilke, P.; Ott, J.; Thorwirth, S.; Hieret, C. *Astron. Astrophys.* **2008**, *482*, 179.
- (19) Arnaud, R.; Adamo, C.; Cossi, M.; Milet, A.; Vallee, Y.; Barone, V. *J. Am. Chem. Soc.* **2000**, *122*, 324.
- (20) Basiuk, V. A. *J. Phys. Chem. A* **2001**, *105*, 4252.
- (21) Koch, D. M.; Toubin, C.; Peslherbe, G. H.; Hynes, J. T. *J. Phys. Chem. C* **2008**, *112*, 2972.
- (22) Maeda, S.; Ohno, K. *Chem. Phys. Lett.* **2004**, *398*, 240.
- (23) Maeda, S.; Ohno, K. *Chem. Lett.* **2004**, *33*, 1372.
- (24) Maeda, S.; Ohno, K. *Astrophys. J.* **2006**, *640*, 823.
- (25) Herbst, E. *Chem. Soc. Rev.* **2001**, *30*, 168.
- (26) Blagojevic, V.; Petrie, S.; Bohme, D. K. *Mon. Not. R. Astron. Soc.* **2003**, *339*, L7.
- (27) Snow, J. L.; Orlova, G.; Blagojevic, V.; Bohme, D. K. *J. Am. Chem. Soc.* **2007**, *129*, 9910.
- (28) Largo, A.; Redondo, P.; Barrientos, C. *Int. J. Quantum Chem.* **2004**, *98*, 355.
- (29) van Dishoeck, E. F.; Jansen, D. J.; Schilke, P.; Phillips, T. G. *Astrophys. J.* **1993**, *416*, L83.
- (30) Mehringer, D. M.; Snyder, L. E.; Miao, Y.; Lovas, F. *Astrophys. J.* **1997**, *480*, L71.
- (31) Jackson, D. M.; Stibrich, N. J.; McLain, J. L.; Fondren, L. D.; Adams, N. G.; Babcock, L. M. *Int. Mass. Spectrom.* **2005**, *247*, 55.
- (32) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
- (33) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358.
- (34) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.
- (35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millan, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.



Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelly, 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.; Baboul, A. G.; 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.; Challa-

combe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian Inc.: Pittsburgh, PA, 1998.

- (36) Lattelais, M.; Ellinger, Y.; Zanda, B. *Int. J. Astrobiol.* **2007**, 6, 37.

CT8002833