

Quantum chemical study of a new reaction pathway for the adenine formation in the interstellar space

V. P. Gupta¹, P. Tandon¹, P. Rawat², R. N. Singh², and A. Singh¹

¹ Department of Physics, University of Lucknow, 226007 Lucknow, India
e-mail: vpgpt1@gmail.com

² Department of Chemistry, University of Lucknow, 226007 Lucknow, India

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ABSTRACT

Gas phase chemistry in the cold interstellar clouds is dominated by ion-molecule and radical-radical interactions, though some neutral-neutral reactions are also barrier-free and efficient at cold temperatures. It has been suggested that it is impossible to synthesize detectable abundances of the pre-biotic HCN oligomer adenine ($\text{H}_5\text{C}_5\text{N}_5$) in the interstellar medium via successive neutral-neutral reactions. We attempted therefore to use quantum chemical techniques to explore if adenine can possibly form in the interstellar space by radical-radical and radical-molecule interaction schemes, both in the gas phase and in the grains. We report results of ab initio calculations for the formation of adenine starting from some of the simple neutral molecules and radicals detected in the interstellar space. The reaction path is found to be totally exothermic and barrier free, which increases the probability of occurrence in the cold interstellar clouds (10–50 K). We also estimated the reaction rates.

Key words. molecular processes – ISM: molecules – astrochemistry

1. Introduction

Astronomers have discovered over the last four decades that the denser clouds in the interstellar medium (ISM) have a complex chemistry involving both particulate water (interstellar grains) and a gas phase in which more than 150 molecular species have been accurately identified (Smith 1988; Langer et al. 2000; Miller & Orgel 1974). In particular, nitriles and nitrile chemistry are found in a variety of astronomical environments (Hudson & Moore 2004). The interstellar chemistry is important because it pertains to the largest objects in the universe whose composition is subject to chemical bonding. Low temperature (often ~ 10 K) and density ($\geq 10^4$ molecules/cm³ in the denser regions) make the interstellar clouds chemistry very interesting (Bale & Bale 2000, 1987). Herbst & Millar (2007) have reviewed the chemical processes that occur in the interstellar cores ($T \approx 10$ K, $N \approx 10^4$ cm⁻³), which are the coldest objects in the larger assemblies of gas and dust known as interstellar clouds. The authors have shown how these processes produce the vast variety of exotic and normal molecules that are detected in these portions of the interstellar medium, both in the gas phase and on the surface of the dust particles. Although much is known about the chemistry of interstellar clouds, much also remains uncertain because of the variety of heterogeneous processes that may be important, including the effect of radiation fields and cosmic rays. Larger and warmer structures known as hot cores and corinos with temperatures ranging from 100–300 K also show a rich chemistry that is quite different from their colder forebears. Thus, while most of the organic species found in cold cores are very unsaturated, the more saturated species are associated with hot cores/corinos (Lis et al. 2006). A rich organic chemistry of molecular clouds leads us to expect even

more complex species of prebiotic interest to be present in the interstellar medium. Numerous experiments have demonstrated that amino acids, nucleotides, carbohydrates, and other essential compounds form under simulated primitive earth conditions from simple starting materials, like HCN, cyano compounds, aldehydes, and ketones etc. (Orgel 2004; Abelson 1966). In a dense molecular cloud, ices are estimated to receive both particle and photon doses on the order of a few eV/molecule. As a result of these radiations, the gas phase molecules of the interstellar medium provide many intriguing examples of nitrile chemistry such as the formation of nitrile/isonitrile pairs (HCN/HNC, $\text{CH}_3\text{CN}/\text{CH}_3\text{NC}$, $\text{HCCCN}/\text{HCCNC}$ etc.), inorganic nitriles (MgCN, NaCN, NH_2CN) and ions and unstable species (HNCCC, CN, HCCN etc.) (Hudson & Moore 2004). HCN, a highly energetic prebiotic precursor, is quite abundant under primitive conditions in the universe and the early earth. The oligomerization of HCN provides an intriguing route to chemical evolution because it may lead to the production of biologically important molecules such as adenine.

Until recently, the speculation about the role of HCN in forming prebiotic molecules had been confined to reactions in solution under conditions of the primitive earth (Oro & Kimball 1962; Sanchez et al. 1968; Levy et al. 2000). However, Chakraborti & Chakraborti (2000) proposed on the basis of modeling calculations that DNA bases can be produced by gas phase reactions in dense interstellar clouds. This view was strongly contradicted by Smith et al. (2001). On the basis of quantum chemical and kinetic techniques, they showed that reaction between two HCN molecules under interstellar conditions cannot efficiently lead to a dimer ($\text{H}_2\text{C}_2\text{N}_2$) and hence it is impossible to synthesize detectable abundances of the HCN oligomer adenine ($\text{H}_5\text{N}_5\text{C}_5$) in the interstellar medium via successive

neutral-neutral reactions between HCN and its dimer, trimer and tetramer. It is, however, suggested that there may be syntheses leading to the formation of amino acids and nuclear bases that involve ion-molecule, radical-molecule or radical-radical reactions (Sorrell 2001; Woon 2002a).

Gas phase chemistry in cold interstellar clouds has to proceed under the constraints of low density and low temperatures which rule out the possibility of three-body processes such as ternary association and ordinary chemical reactions that possess a significant amount of activation energy. The very low particle density that leads to long intervals between collisions combined with very low rate coefficients for activation energies ≥ 1 eV at very low temperatures (about 10 K), based on the Arrhenius expression, do not allow these reactions to happen. The chemical processes that dominate the gas phase chemistry under such conditions are thus exothermic reactions without activation energy. Ion-molecule and radical-radical interactions dominate the gas-phase chemistry in the cold interstellar clouds (Herbst 2005), though some neutral-neutral reactions such as $\text{CN} + \text{C}_2\text{H}_2$ and $\text{C}_2\text{H} + \text{C}_2\text{H}_2$ (Woon & Herbst 1997; Herbst & Woon 1997) are also barrier free and efficient at cold temperatures. These fast ion-molecule and radical-radical reactions have rate coefficients typically in the range 10^{-9} – 10^{-11} $\text{cm}^3 \text{s}^{-1}$, which is several orders of magnitude higher than those with barriers and 10–100 times higher than those for neutral-neutral reactions without activation energy at temperatures as low as 10 K. Reactions involving ions and non-polar neutrals often follow a very simple expression for the rate constant that was first derived by Langevin (Herbst 1996). A more accurate theory of bimolecular reaction dynamics in the gas phase using a quantum dynamical approach has also been suggested (Clary 2008). Calculations with this approach can be made for reactions involving up to four atoms, but more approximate methods are normally needed for more complicated reactive systems. Bates (1983) developed a theory of molecular formation by radiative association in the interstellar clouds that explicitly incorporates the long-range attraction between the reactants. Bates also suggested a very simple semiempirical formula for the rate coefficients for radiative association at 30 K and a method to calculate its upper limit. The chemistry of interstellar clouds is, however, not limited to the gas phase. It can occur on grain surfaces or within the ice mantles. Several studies of ice-bound processes have been performed in search of other key and possible collateral reactions relevant to astrochemistry and astrobiology (Woon 2002b). No studies related to radical-radical or radical-molecule interactions have been reported so far for the adenine formation in the interstellar space.

In the present communication we are reporting the results of an ab initio calculation for the formation of adenine starting from some of the molecules detected in the interstellar space. We adopted radical-radical and radical-molecule interaction schemes in the gas phase and in the grains. The reaction path is totally exothermic and does not involve potential barriers, which increases the probability of occurrence. An estimate of the rate coefficients for the various reactions was made as well.

2. Methodology

Computations were performed based on the B3LYP density functional theory with the 6-31G** basis set. The 6-31G** basis set is widely used in chemistry because it succeeds in reproducing experimental data with high reliability (Cramer 2002). All calculations were carried out with the Gaussian 03 W program. Total energies, zero point vibrational energy (ZPVE) and

electronic energies (EE) of all molecules/radicals formed during the reaction path toward the formation of adenine were calculated and are given in Table 1. We used the polarizable continuum model (PCM) as implemented in the Gaussian 03 program to include the bulk solvation effect. The PCM “bulk solvent medium” is simulated as a continuum of the dielectric constant ϵ ($=78.5$). This surrounds a solute cavity, which is defined by the union of a series of interlocking spheres centered on the atoms. Harmonic frequency calculations were also conducted to identify the stable states. Because all chemical reactions involved in the present study are exothermic and barrierless and do not follow the temperature-dependent Arrhenius expression, an estimate of the rate coefficient at 30 K was made on the basis of the semiempirical relationship developed by Bates (1983)

$$k = 1 \times 10^{-21} A_r (6E_0 + N - 2)^{3N-7} / (3N - 7)! \text{ cm}^3 \text{ s}^{-1}, \quad (1)$$

where E_0 is the association energy in eV, A_r is the transition probability in s^{-1} (taken as 100), and N is the number of nuclei in the complex. The limit is adopted if the calculated value exceeds the limit set by the equation

$$k = 7.41 \times 10^{-10} \alpha^{1/2} (10/\mu)^{1/2} \text{ cm}^3 \text{ s}^{-1}, \quad (2)$$

where α is the polarizability in \AA^3 and μ is the reduced mass of the reactants on the ^{12}C amu scale, as suggested by Bates (1983). The results are given in Table 2.

3. Result and discussion

The radical reactions are mainly of two types, viz. (a) unimolecular reactions such as fragmentation and rearrangement; (b) bimolecular reactions between radical and molecules, such as addition, displacement, atom abstraction etc. Out of these reactions, the addition, displacement (substitution), and rearrangements are important and more common where radicals are used as either reactants or intermediates. The reaction leading to the adenine formation in the interstellar space involves several simple neutral molecules and radicals such as HCN (Jiurys 2006), HCCN (Guelin & Cernicharo 1991), NH_2CN (Turner et al. 1975), and CN (Fuente et al. 2005), and belongs to the second category in which both addition and atom abstraction take place. We found that the formation of adenine in the gas phase as well as in the water containing icy grains takes place in six steps. The reaction pathways are given in Table 2, which also contains computed reaction energies and estimated reaction coefficients in the gaseous phase. The steps of formation of adenine are schematically shown in Fig. 1. No transition states could be located in the reaction path. Optimized geometries of the reactants and products at B3LYP/6-31G** level are given in Fig. 2. The mechanism of adenine formation can be considered under the following headings.

3.1. Formation of the five-membered ring

The five-membered ring of adenine may be formed in the interstellar space through a barrier less exothermic reaction between hydrogen cyanide (HCN) and cyanocarbene (HCCN), both of which are known to exist in high concentrations in space (Jiurys 2006; Guelin & Cernicharo 1991). Both HCN and its isomer HNC are found to be widely spread in space (Snyder & Buhl 1971; Boonman et al. 2001; Charnley et al. 2001). Their relative abundance varies a great deal in the ISM with an inverse temperature dependence: in dark clouds the ratio is typically ≥ 1 ,

Table 1. Electronic (EE), zero point vibrational (ZPVE) and total energies of molecules and radicals in the gas phase and ice bound reactions (PCM) based on B3LYP/6-31G** calculations.

Molecules/ TS/Radicals	Energies in gas phase (a.u.)			Energies in PCM (a.u.)		
	E.E.	ZPVE	Total	E.E.	ZPVE	Total
H	-0.500273	0.00000	-0.500273	-0.500273	0.000000	-0.500273
CN	-92.711747	0.004922	-92.706825	-92.713838	0.004928	-92.708911
HCN	-93.424575	0.014673	-93.409901	-93.434216	0.016126	-93.418090
HNC	-93.399423	0.014303	-93.385121	-93.413563	0.014863	-93.398699
HCCN	-131.396973	0.018161	-131.378812	-131.405225	0.017969	-131.387256
NH ₂ CN	-148.787012	0.034118	-148.752894	-148.806786	0.033024	-148.771753
HCN+HCCN	-224.821548	0.032834	-224.788713	-224.839441	0.034095	-224.805346
Molecule1	-224.856126	0.043729	-224.812397	-224.865374	0.043284	-224.822091
Molecule2	-225.526958	0.058598	-225.468359	-225.544759	0.057524	-225.487235
Molecule2 +NH ₂ CN	-374.313970	0.092716	-374.221253	-374.351545	0.090548	-374.258988
Molecule3	-374.389074	0.097919	-374.291155	-374.416930	0.095909	-374.321021
Molecule3 +CN	-467.100821	0.102841	-466.997980	-467.130768	0.100837	-467.029932
Molecule4	-467.241602	0.110218	-467.131384	-467.284651	0.108845	-467.173986
Molecule5	-467.863780	0.120475	-467.743305	-467.897499	0.117811	-467.779687
Molecule5 +CN	-560.575527	0.125397	-560.450130	-560.611337	0.122739	-560.488598
Molecule6a	-560.751869	0.129982	-560.621887	-560.782123	0.126886	-560.655237
Molecule6b	-560.768530	0.129972	-560.638558	-560.798449	0.127699	-560.670750
Molecule7 (Adenine)	-467.352446	0.115679	-467.236766	-467.368560	0.112023	-467.256537

Table 2. Computed reaction energies and estimated rate coefficients for the formation of adenine.

S. No.	Reaction steps	Reaction Energies (kcal/mol) ^a		Rate Coefficients (cm ³ s ⁻¹) Gas phase
		Gas phase	PCM	
1	HCN+HCCN → Molecule 1	-21.69 (-14.86)	-16.27 (-10.51)	2.13×10^{-17b}
2	Molecule 1 + H → Molecule 2	-107.03 (-97.69)	-112.39 (-103.46)	7.96×10^{-9b}
3	Molecule 2 + NH ₂ CN → Molecule3	-47.13 (-43.86)	-41.03 (-38.93)	6.24×10^{-12b}
4	Molecule 3 + CN → Molecule 4	-88.34 (-83.71)	-96.56 (-90.39)	1.80×10^{-9c}
5	Molecule 4 + H → Molecule 5	-76.50 (-70.06)	-70.56 (-66.16)	8.71×10^{-9c}
6	(a)Molecule 5 + CN → Molecule 6a (adenine+HNC)	-110.65 (-107.78)	-107.17 (-104.57)	1.89×10^{-9c}
	(b)Molecule 5 + CN → Molecule 6b (adenine+HCN)	-121.11 (-118.24)	-117.41 (-114.30)	1.91×10^{-9c}

Notes. ^(a) Energy difference in kcal/mol, with zero point corrected values in parentheses. ^(b) Semiempirical values at 30 K (Eq. (1)). ^(c) Upper limit (Eq. (2)).

whereas in hot cores it is lower. Based on this temperature dependence HCN is presumed to be a component of interstellar ices (Boonman et al. 2001). It has a fractional abundance of about 5.89×10^{-9} with regard to H₂ in dark interstellar clouds (Woodall et al. 2006). HCCN is found to be present in cold (Herbst & Millar 2007) and hot interstellar clouds. A radical with unusual allenic structure, it is found to be about twice as abundant as the stable species CH₃CN (Remijan et al. 2005) in the circumstellar envelope IRC+10216, but much less in the giant clouds Sgr B2 and, Orion. In the cold interstellar clouds, its

fractional abundance is expected to be about 2.78×10^{-11} with regard to H₂.

The HCCN molecule can have two possible geometries, a linear equilibrium geometry for the triplet electronic ground state and a bent structure consistent with the accepted name “cyanocarbene”. While initial studies of this molecule believed the linear geometry to be the most plausible structure (Saito et al. 1984), theoretical studies by Kim et al. (1983) have suggested that a bent equilibrium geometry is more stable than the linear geometry by about 2.5 kcal/mol. Finally it has been confirmed by

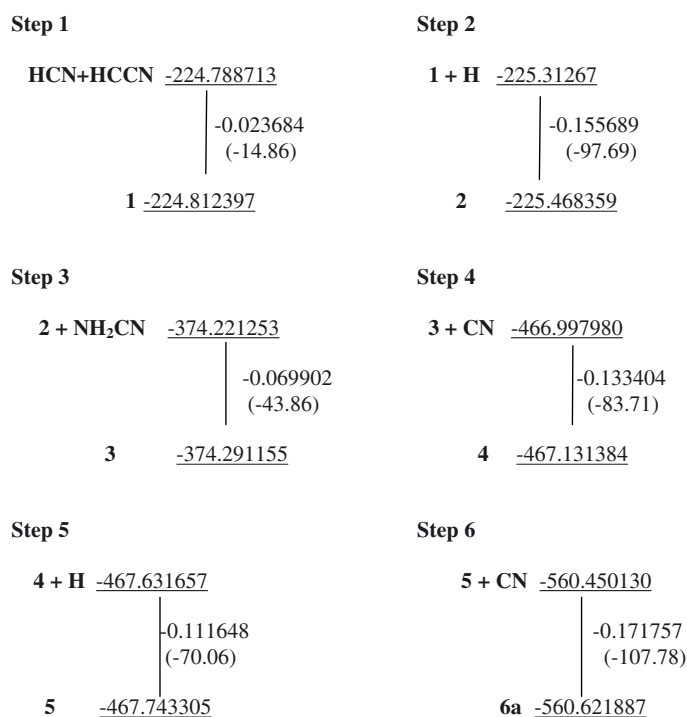


Fig. 1. Steps of adenine formation and energy level diagram. Energy differences with ZPVE are in a.u. (energy differences with ZPVE in kcal/mol are given in parentheses).

Rice & Schaefer (1987) on the basis of multiconfiguration SCF (MC-SCF) studies using DZP and TZ2P basis sets that the bent structure lies 6.2 and 5.7 kcal/mol, respectively, below the linear conformation. Our studies show that the ring closure leading to the five-membered ring is possible only with the bent conformation of the HCCN molecule. The reaction between the highly reactive carbene structure of HCCN and HCN leads to the formation of molecule 1 (1,2 dihydro imidazole) for which the optimized structure is given in Fig. 2. In this process, the carbon atom C2 (charge +0.159) of HCN (Fig. 2a) becomes attached to the nitrogen atom N2 (charge -0.403) of HCCN (Fig. 2c), while atom N3 of HCN gets attached to atom C3 of HCCN, which has two free electrons in its carbene structure. The reaction energy for this process is -21.69 kcal/mol in the gas phase; with ZPVE correction, the energy is -14.86 kcal/mol (Table 2). The rate coefficient for this radiative association reaction is estimated to be $2.13 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ in the gas phase (Table 2).

In an exothermic addition reaction, molecule 1 picks up a hydrogen atom, which leads to another five-membered ring molecule 2 (2,3 dihydro-1H-imidazole radical, Fig. 2e) and releases an energy of -107.03 kcal/mol (-97.69 kcal/mol with ZPVE correction). Molecule 2 is a very reactive molecule and acts as a nucleophile in further reactions.

3.2. Formation of six-membered pyrimidine ring

The pyrimidine ring of adenine may be formed in a two step reaction (steps 3 and 4 in Table 2) that involves cyanamide (NH_2CN) and a cyanide radical. CN is a very common interstellar species and was the first to be detected in the interstellar clouds (McKellar 1940). It has been observed in both diffuse clouds and dense clouds (Liszt & Lucas 2001). While the CN radical has a fractional abundance of 1.04×10^{-11} , the neutral NH_2CN molecule has a steady-state fractional

abundance of 2.02×10^{-10} with regard to H_2 in the dark interstellar clouds (Woodall et al. 2006). Cyanamide contains nucleophilic and electrophilic sites within the same molecule and exists in two tautomeric forms, one with the connectivity NCNH_2 and the other with the formula HNCNH (diimide tautomer). In the formation of the pyrimidine ring (step 3), the NCNH_2 form (Fig. 2d) dominates. In the interstellar space, as the quantum chemical calculations show, the NCNH_2 form of cyanamide may react with molecule 2 to give rise to molecule 3 (4 carboxaimidine-1H-imidazole radical) with a reaction energy of -47.13 kcal/mol (Table 2); this energy is -43.90 kcal/mol with ZPVE correction. The carbon atom (C11) of NH_2CN forms a single bond with a length of 1.482 Å with the carbon atom (C1) (Fig. 2g) of the five-membered ring, which results in significant changes in the molecular geometry and a 1,3-electron transfer from C1 to N13. The rate coefficient for this reaction is estimated to be $6.24 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ in the gas phase (Table 2).

The next step (step 4, Table 2) in the formation of the pyrimidine ring involves the closure of the incomplete ring of molecule 3 to yield molecule 4 (2,4 dihydro-3H-purine-6-amine) through the addition of a cyanide radical which is quite abundant in the interstellar space (Fuente et al. 2005). The Mulliken population analysis of molecule 3 gives net atomic charges of +0.073 and -0.465 e.s.u. at C3 and N13. These atoms can have electrostatic attraction toward the N14 and C15 atoms of the CN radical with net charges -0.226 and +0.226 e.s.u. (not shown in the figure), respectively, and can facilitate the six-membered ring closure. The addition of CN radical is an exothermic reaction with a reaction energy -88.34 kcal/mol (Table 2). The reaction path is shown in Fig. 1. Besides the ring closure, the reaction also involves a hydrogen-atom transfer from carbon atom C3 to the nitrogen atom N14. This leads to the formation of the stable molecule 4, whose optimized geometry is given in Fig. 2. This is a faster reaction than step 3 with an estimated rate coefficient $1.80 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ in the gas phase (Table 2).

The carbon atom C15 in molecule 4 is a divalent atom attached to two electronegative nitrogen atoms which make it more electron deficient. It therefore presents a highly reactive site that can easily combine with a hydrogen atom to form the C15H16 bond and generate molecule 5 (6 amino-3H-purine radical, Fig. 2i). The reaction energy for this step is -76.5 kcal/mol (step 5 in Table 2).

3.3. Formation of adenine

In the last step (step 6, Table 2) of the reaction process we explored the reaction of molecule 5 (6 amino-3H-purine radical) with a cyanide radical. The CN radical may cause the removal of the hydrogen atom from molecule 5 in two ways: (a) through the formation of HNC molecule leading to molecule 6(a) (adenine + HNC), or (b) through the formation of HCN molecule leading to molecule 6(b) (adenine + HCN). Both processes are barrierless and exothermic with reaction energies (corrected with ZPVE) of -107.78 kcal/mol and -118.24 kcal/mol, respectively. The rate coefficient for step 6, which leads to the formation of molecule 6(a), has a limit of $1.91 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, and that leading to molecule 6(b) has a limit of $1.89 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ in the gas phase (Table 2). Thus, the reaction that leads to adenine formation with the release of HNC is comparatively faster than the one with the release of HCN. Some of the geometric parameters of adenine are given in Fig. 2. These are found to agree well with the experimental (Vogt et al. 2009) and calculated (Sponer & Hobza 1994) values reported in the literature.

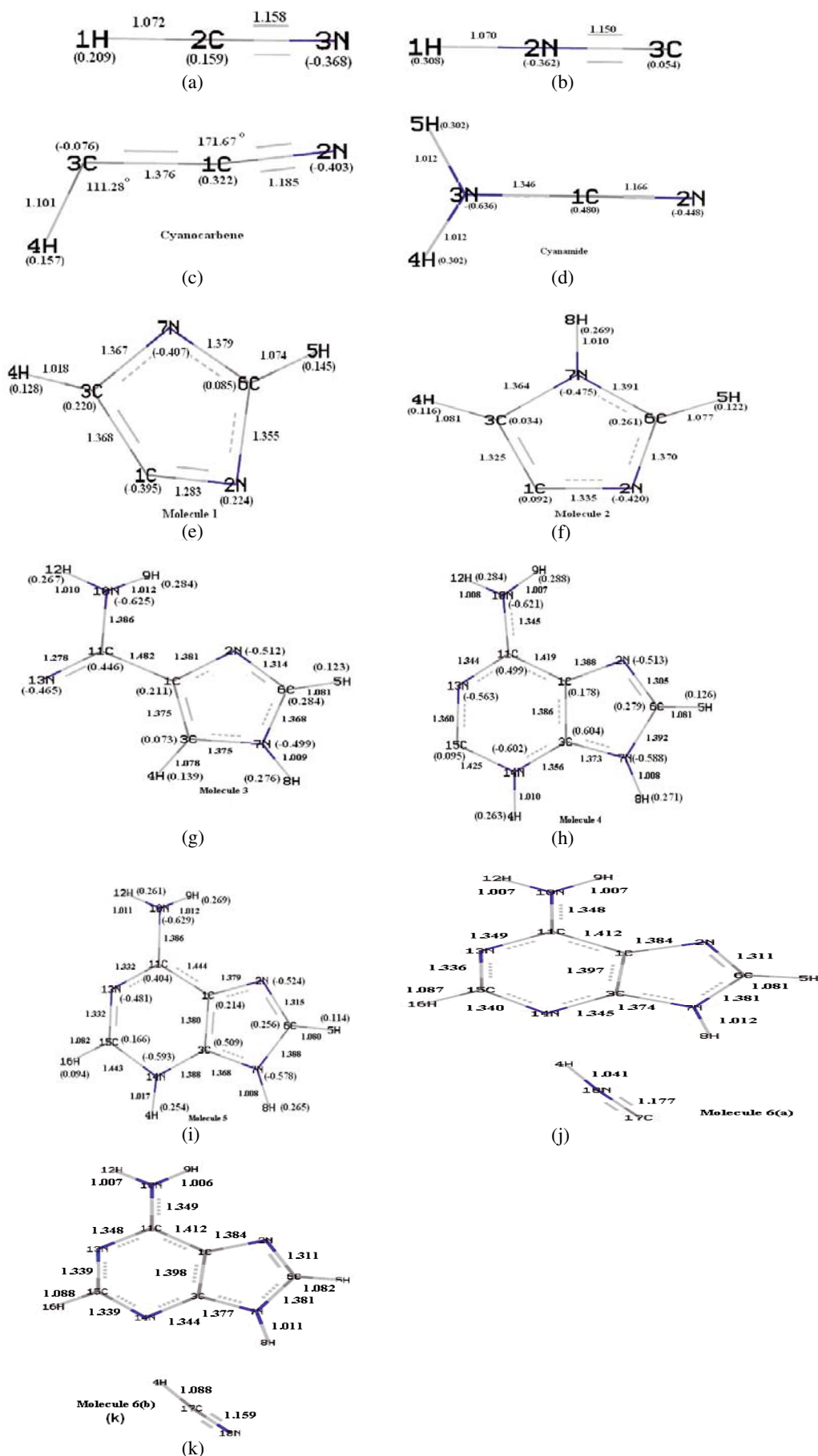


Fig. 2. Geometries of reactants and products in the adenine formation (charge densities are shown in parentheses).

4. Effect of solvent on reaction mechanism

It is known that ice mantles may coat interstellar or circumstellar dust grains under certain conditions, whereby they provide sites where the chemistry can be quite different from that which prevails in the gas phase (Herbst 1993; Ehrenfreund & Fraser 2003). Characterizing the range of chemical behavior that can occur on or within ice mantles is therefore essential for a full understanding of the nature and evolution of the gas and condensed phase composition in interstellar objects and elsewhere. We attempted to study the adenine formation in ice-grains, which were treated as a bulk solvent (water). The influence of the bulk solvent on the energetics of chemical reactions was analyzed with the polarizable continuum model (PCM) with dielectric constant 78.5. The electronic energies and zero point vibration energies (ZPVE) from B3LYP/6-31G** calculations are given in Table 1, and the reaction energies for the different reaction steps are given in Table 2.

Table 1 shows that the solvent tends to lower the energies of the reactants and their products by as much as 24 kcal/mol. This also changes the reaction energy up to 8 kcal/mol. All reactions in the solvent remain exothermic and do not encounter a potential barrier. This shows that all reactions in the icy grains may lead to the adenine formation with high probability.

5. Conclusions

The possibility of adenine formation from some of the simpler molecules such as HCN, HCCN, NH₂CN, and CN, which are known to be abundant in the interstellar space was explored with quantum chemical methods that use radical-radical and radical-molecule interaction schemes in the gas phase and in the grains. We adopted the PCM model to study the reaction in the grains, which were simulated as a continuum of dielectric constant ϵ (=78.5). We calculated the total energies, zero point vibrational energies (ZPVE) and electronic energies (EE) of all molecules/radicals formed during the reaction path. The molecular geometries of the reactants, and their products were optimized and the harmonic frequencies were calculated to identify the stable states. The study of the reaction energies and the structures of the reactants and products shows that the adenine formation is possible in the gas phase as well as in the water icy grains in six steps. The reaction paths in the gas phase and in the solvent are totally exothermic and do not involve potential barriers. This increases the probability of occurrence of the reactions under the conditions of the interstellar space; the upper limit of the rate coefficient is $8.71 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

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