A Computational Study of the Reaction $N(^2D) + C_6H_6$ Leading to Pyridine and Phenylnitrene

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Abstract. The reaction between nitrogen atoms in their first electronically excited state ^2D with benzene has been characterized by electronic structure calculations of the stationary points along the minimum energy path. We focused our attention, in particular, to the two channels leading to C_6H_5N (phenylnitrene) + H and C_5H_5N (pyridine) + CH, due to the relevance of these products. The minima along these reaction paths have been characterized using different ab initio methods in order to find a reasonable compromise between chemical accuracy and computational costs. Our results suggest that, while for geometry optimizations even relatively low level calculations are adequate, for energies higher level calculations are necessary in order to obtain accurate quantitative results.

Keywords: Ab initio calculations · Titan atmosphere · Chemistry of planetary atmospheres · Prebiotic chemistry · Astrochemistry

1 Introduction

The atmosphere of Titan, the largest moon of Saturn [1], is believed to be in some way reminiscent of the primordial atmosphere of Earth [2, 3], being composed mainly by dinitrogen, methane, simple nitriles like HCN and HCCCN, simple hydrocarbons like C_2H_6, C_2H_4 and C_2H_2, H_2 and Ar. Dinitrogen is the prevalent species, being the 97% of the atmosphere and the second relevant constituent is CH_4 which represents an average amount of 2.7%. All the other species are present only in trace amounts, but their reactivity is very important as suggested by the plethora of information provided

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by the NASA/ESA/ASI Cassini-Huygens mission [4]. Recent investigations suggested also the presence of positive ions [1, 5, 6] and negatively charged ions [7] in Titan's ionosphere. More recent information were provided by the observations performed with the ALMA interferometer [8]. Among the species identified by Cassini Ion Neutral Spectrometer (INMS), benzene shows a relatively important mole fraction, being 1.3×10^{-6} at 950 km [9]. However, the low number density and low temperature conditions (94 K at the surface and up to 200 K in the upper atmosphere of Titan [2, 4]) do not allow reactivity among neutral closed shell molecules because of the presence of relatively high activation energy barriers. In the range of altitude where benzene is present, however, molecular dinitrogen is converted into atomic nitrogen or ions by energetic processes [10] or by the interaction with Extreme Ultra-Violet (EUV) radiation. The dissociation of molecular dinitrogen induced by dissociative photoionization, galactic cosmic ray absorption, N_2^+ dissociative recombination, or dissociation induced by EUV photons produces atomic nitrogen in its electronic ground state ^{4}S and in the first excited ^{2}D state in similar amounts [10]. Atomic nitrogen in its ^{4}S ground state exhibits very low reactivity with closed shell molecules. On the contrary, atomic nitrogen in its first electronically excited ^{2}D state shows a significant reactivity with several molecules identified in the atmosphere of Titan. Atomic nitrogen in its excited ^{2}D state is metastable but it shows a radiative lifetime long enough to react in binary collisions with other constituents of the upper atmosphere of Titan [11–19]. We have already investigated the reactions of atomic nitrogen in its excited ^{2}D state with various hydrocarbons, like CH_4, C_2H_2, C_2H_4, C_2H_6, in laboratory experiments by the crossed molecular beam technique with mass spectrometric detection and time-of-flight analysis at different collision energies complemented by ab initio and kinetics calculations [20–25]. More recently, with the same approach, we have investigated the reaction between N(^{2}D) and benzene [26] which is supposed to be very relevant in the upper atmosphere of Titan, from the stratosphere up to the thermosphere where the first haze layer is located.

The study of the potential energy surface of the system N(^{2}D) + C_6H_6 [26] showed the presence of many exit reactive channels as well as many isomeric species with seven atoms of the second period and 6 hydrogen atoms and a total of 49 electrons. The ab initio study of these systems is computationally very challenging and a compromise between chemical accuracy and computational resources is necessary. In this manuscript we focus our attention on two of the main exit channels of the reaction between N(^{2}D) and benzene, *i.e.* the formation of pyridine and phenylnitrene. We used different computational approaches in order to check if relatively simple calculations are sufficiently reliable.

2 Computational Details

The reactive channels of the N(^{2}D) + C_6H_6 system leading to phenylnitrene and pyridine were investigated by locating the lowest stationary points at the B3LYP level of theory [27, 28], in conjunction with the 6-311+G** basis set [29, 30], on the doublet ground state potential energy surface. At the same level of theory we have computed the harmonic vibrational frequencies in order to check the nature of the stationary

points, *i.e.* minimum if all the frequencies are real, saddle point if there is only one imaginary frequency. The assignment of the saddle points was performed using intrinsic reaction coordinate (IRC) calculations [31, 32] The geometry of all the species was optimized without any symmetry constraints considering for all the investigated species the electronic ground state. In order to check the accuracy of the computed geometries, we have optimized all the minima using a more extended basis set. We have optimized all the minima at the B3LYP level [27, 28] with the correlation consistent aug-cc-pVTZ basis set [33]. For selected systems, the energy was computed also at the higher level of calculation CCSD(T) [34–36] using the same correlation consistent aug-cc-pVTZ basis set [33] and the B3LYP/aug-cc-pVTZ optimized geometries, following a well established computational scheme [37–41]. The accuracy of the employed approach, in particular as far as basis set completeness is concerned, has been recently investigated [42]. Both the B3LYP and the CCSD(T) energies were corrected to 0 K by adding the zero point energy correction computed using the scaled harmonic vibrational frequencies evaluated at B3LYP/aug-cc-pVTZ level. The energy of $N(^2D)$ was estimated by adding the experimental [43] separation $N(^4S) - N(^2D)$ of 55 kcal mol^{-1} to the energy of $N(^4S)$ at all levels of calculation. All calculations were done using Gaussian 09 [44] while the analysis of the vibrational frequencies was performed using Molekel [45, 46].

3 Results and Discussion

Figure 1 reports the main steps along the minimum energy paths leading to pyridine and phenylnitrene starting from the $N(^2D) + C_6H_6$ reactants, computed at the B3LYP/6-311+G** level. Table 1 reports the energy changes and barrier heights computed at the same level of theory for the processes leading to pyridine and phenylnitrene. We can notice that, while we have only one path leading to pyridine, we have three different paths leading to phenylnitrene. All the reported energies are relative to $N(^2D) + C_6H_6$. We can notice that all the minima, as well as the transition states, lie under the energy of the reactants. The interaction of $N(^2D)$ with C_6H_6 gives rise to the van der Waals adduct **C_6H_6N (1)** more stable than the reactants by 30.1 kcal/mol, which evolves, through a barrier of only 2.5 kcal/mol, to minimum **C_6H_6N (2)** more stable than the reactants by 52.1 kcal/mol. **C_6H_6N (2)** can dissociate an hydrogen atom giving rise to phenylnitrene **C_6H_5N (10)** in its triplet ground state, through a barrier of 25.9 kcal/mol, or isomerizes to the more stable species **C_6H_6N (3)** in a process which shows almost no barrier (0.1 kcal/mol). **C_6H_6N (3)** can isomerize to **C_6H_6N (4)** through a barrier of 17.3 kcal/mol. **C_6H_6N (4)** isomerizes to **C_5H_5NCH (5)** through a barrier of 20.1 kcal/mol, which isomerizes to **C_5H_5NCH (6)** through a barrier of 22.8 kcal/mol. **C_5H_5NCH (6)** dissociates into pyridine (**7**) and CH, in a process endothermic by 56.4 kcal/mol. Alternatively **C_6H_6N (3)** can isomerize to **C_6H_5NH (9)** through a relatively high barrier of 48.4 kcal/mol. **C_6H_5NH (9)** then dissociates into phenylnitrene and hydrogen in an endothermic process (85.8 kcal/mol) without any barrier. Phenylnitrene can be formed also through species **C_6H_6N (8)** which can be formed from species **C_6H_6N (2)**.

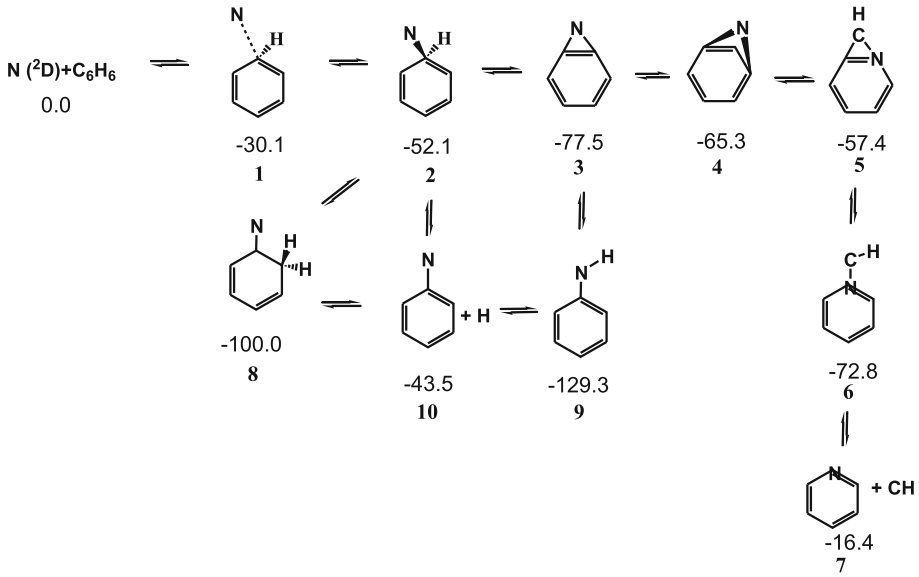

Fig. 1. Main steps along the minimum energy path for the channels leading to phenylnitrene and pyridine. Relative energies (kcal/mol, 0 K) with respect to the reactants N+C_6H_6 computed at B3LYP/6-311+G** level.

The species reported in Fig. 1 are only some of the possible isomers that can be formed starting from N(^{2}D) and C_6H_6 [26]. The chemistry of this reaction indeed is very complex.

Table 1. Enthalpy changes and barrier heights (kcal/mol, 0 K) computed at the B3LYP/6-311+G** level of theory for selected dissociation and isomerization processes for the system N(^{2}D) + C_6H_6. When indicated, the superscript represents the spin multiplicity.

	ΔH_0^0	Barrier height
N(^{2}D) + C_6H_6 → C_6H_6N (1)	−30.1	
C_6H_6N (1) → C_6H_6N (2)	−22.0	2.5
C_6H_6N (2) → C_6H_6N (3)	−25.4	0.1
C_6H_6N (3) → C_6H_6N (4)	12.2	17.3
C_6H_6N (4) → C_5H_5NCH (5)	7.9	20.1
C_5H_5NCH (5) → C_5H_5NCH (6)	−15.4	22.8
C_5H_5NCH (6) → C_5H_5N (7) + CH	56.4	
C_6H_6N (2) → C_6H_6N (8)	−47.9	11.4
C_6H_6N (8) → $^3C_6H_5N$ (10) + H	56.5	
C_6H_6N (3) → C_6H_5NH (9)	−51.8	48.4
C_6H_5N (9) → $^3C_6H_5N$ (10) + H	85.8	
C_6H_6N (2) → $^3C_6H_5N$ (10) + H	8.6	25.9

We performed a fist study of this system at the B3LYP/6-311+G** level since the size of these systems is relatively large and more accurate calculations are very expensive. However, B3LYP/6-311+G** results could be not enough accurate to study these systems. In order to check this point, we optimized all the investigated minima at the B3LYP/aug-cc-pVTZ level. In Fig. 2 we have reported the main steps along the minimum energy path for the channels leading to pyridine and phenylnitrene, with the relative energies computed at this level of calculation, while in Fig. 3 we have reported the geometries of the investigated species computed at the B3LYP/6-311+G** level and (in parentheses) those obtained at the B3LYP/aug-cc-pVTZ level. We can notice that the differences both in bond lengths and bond angles are very small. We have only a significant difference in species **C_6H_6N (1)** for the distance between carbon and nitrogen, which is 3.044 Å at B3LYP/6-311+G** level and 3.186 Å at B3LYP/aug-cc-pVTZ level. However, this is not a bond length. It is only a van der Waals interaction which is not very sensitive to the distance. Moreover, we should mention that van der Waals adducts are not very well described by the B3LYP approach, but this is not so relevant in the investigated potential energy surface since this adduct is very stabilized with respect to the reactants.

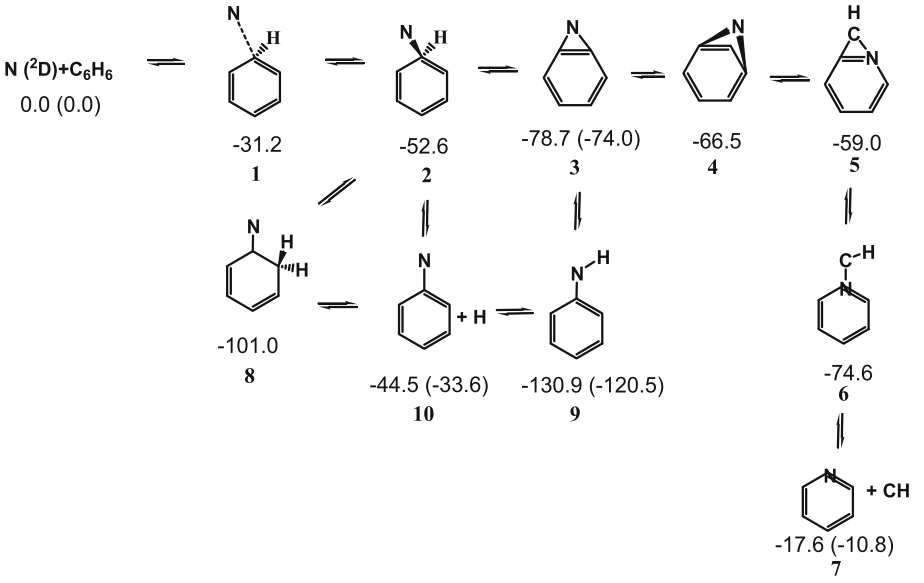

Fig. 2. Main steps along the minimum energy path for the channels leading to phenylnitrene and pyridine. Relative energies (kcal/mol, 0 K) with respect to the reactants $N+C_6H_6$ computed at B3LYP/aug-cc-pVTZ level. Values in parentheses are computed at CCSD(T)/aug-cc-pVTZ level

Since the geometries computed at B3LYP/6-311+G** and B3LYP/aug-cc-pVTZ level are very similar, we expect to have also similar energies with the two approaches. Comparing the results reported in Fig. 2 with those reported in Fig. 1, we can notice that the energy values differ by less than 2 kcal/mol. We can conclude that, as far as geometries are concerned, also the less expensive B3LYP/6-311+G** approach can be accepted.

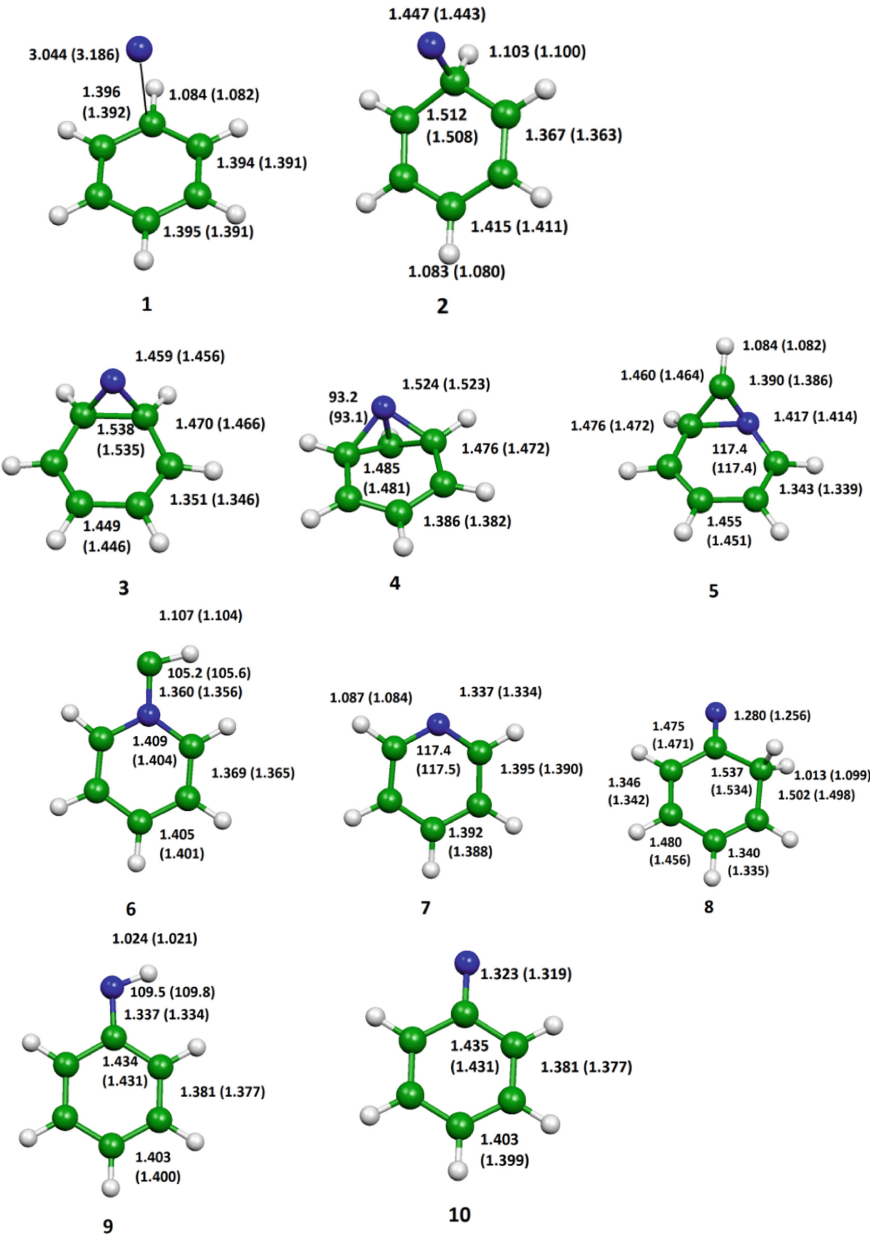

Fig. 3. Optimized geometries at B3LYP/6-311+G** level of the stationary points considered along the minimum energy paths leading from N(^{2}D) + C_6H_6 to pyridine and phenylnitrene. Bond lengths in Å, angles in degrees. Values in parentheses are computed at B3LYP/aug-cc-pVTZ level.

In order to check also the accuracy of the energies, we performed CCSD(T)/aug-cc-pVTZ calculations for selected systems. In particular we computed at this level of calculation the reactants, the intermediates **C_6H_6N (3)** and **C_6H_5NH (9)** and the products pyridine and phenylnitrene in its triplet ground state. In Fig. 2 these results are reported in parentheses. We can notice that the differences between the two approaches can be as high as 10 kcal/mol. In particular, we have a difference of 10.9 kcal/mol for phenylnitrene in its triplet ground state. We should take into account this point, whenever a small energy difference is involved.

4 Conclusions

The study at ab initio level of the two channels of the reaction between nitrogen atoms in their doublet excited state and benzene leading to C_6H_5N (phenylnitrene) + H and C_5H_5N (pyridine) + CH, performed using different methods in order to find a reasonable compromise between chemical accuracy and computational costs suggests that, while for geometry optimizations even relatively low level calculations are adequate, for energies calculations of higher level are necessary in order to obtain accurate quantitative results.

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