MODELING ELECTROCATALYTIC ACTIVITY OF NITROGEN RADICALS

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It has recently been shown that nitrogen radicals electrochemically deposited on carbon nanotube paper can catalyze reactions at the cathode of fuel cells. Density functional theory (DFT) is used to show that O_2 and HO_2 could adsorb on nitrogen radicals such as N_2^-, N_4^-, and N_8^-.The bond dissociation energy to remove an O atom from O_2 and OH from HO_2 bonded to these radicals is calculated. The results show that N_4^- and N_8^- could be effective catalysts for the HO_2 dissociation but not O_2 dissociation. The results support the previous conclusion that N_8^- could be a catalyst for the reactions at the cathode of fuel cells.

Key words: catalysis, nitrogen radicals, oxygen reduction reaction, fuel cells.

I INTRODUCTION

Presently platinum is used to catalyze the reactions that produce H_2O at the cathode of fuel cells. Platinum is expensive and susceptible to time dependent drift and CO poisoning.[1,2] These issues are significant obstacles to the development of large scale commercial application of fuel cells. Likely reactions that produce H_2O at the cathodes are the O_2 dissociation followed by atomic oxygen undergoing the following reaction,

$$2O + 4H^+ + 4e \rightarrow 2H_2O \qquad (1)$$

Another possibility is the formation of HO_2 which bonds to the catalyst followed by the removal of OH which could then undergo the following reaction,

$$OH + H^+ + e \rightarrow H_2O \qquad (2)$$

The object of this paper is to use theoretical methods such as Density Functional Theory (DFT) to determine whether nitrogen radicals can catalyze these reactions. Modeling has been used to understand the role of platinum as a possible catalyst.[3,4] It also has been employed to predict possible new catalysts. For example molecular orbital theory has been used to predict that nitrogen doped graphene, coronene and pentacene could be an effective catalysts .[5,6,7]

It has been shown that electrolysis of sodium azide solutions can be used to deposit nitrogen molecules on carbon nanotube paper.[8] The carbon nanotube paper having the deposited nitrogen molecules was shown by cyclic voltammetry to be an effective catalyst for the ORR reaction in fuel cells. Based on the agreement of density functional calculations of frequencies with measured Raman and IR values of the radicals deposited on the carbon nanotube paper, it was concluded that N_8^- was responsible for the catalytic effect.[8] Because N_8^- has an unpaired electron, It has an available bond to connect with O_2 and HO_2 and is a plausible candidate as a catalyst.. Other possibilities are N_4^- and N_3^0 . The N_4^- radical has been detected in uv photolyzed monovalent azides by electron paramagnetic resonance and has been shown to be stable above room temperature.[,9,10,11] The N_2- has also been observed in irradiated azides but is not stable at room temperature.[12]

Modeling potential catalytic materials for fuel cells involves identifying a material X that bonds to O_2 or HO_2 to form X-O_2 or X- HO_2 such that the bond dissociation energy (BDE) to produce O or OH is less than the BDE to dissociate free O_2 or HO_2. This approach has been used to obtain understanding of the mechanism of platinum catalysis and the modeling of nitrogen doped graphene and coronene as a cathode catalyst in fuel cells.[5,6,7]

II METHODS

The structures at minimum energy of XO_2 , XO, and X HO_2 where X is N_2^- , N_4^- , and N_8^- are calculated using DFT. Imaginary frequencies are identified in the output of the calculations by minus signs and if present indicate the obtained structure is not at a minimum on the potential energy surface. The calculations are performed using the Gaussian 03 software package at the B3LYP/6-31 G* level.[13] The BDE is defined as ,

$$BDE = [E(XO) + E(Z)] - [E(XY)] \qquad (3)$$

where Y is O_2 or HO_2 and Z is O or OH. E is the total electronic energy plus the zero point energy (ZPE) of the minimum energy structure. The ZPE is the total ZPE of all of the normal modes of vibration given by,

$$E_{zpe} = (1/2)h \sum_{i}^{3N-6} f_i \qquad (4)$$

where f_I are the vibrational frequencies of the normal modes and N the number of atoms in the molecule. The calculated BDE given by equation 3 is compared with that to dissociate free O_2 or HO_2. If it is significantly less, it can be argued that X is a good catalyst for the reactions.

Another issue that needs to be considered in assessing these radicals as catalysts for the reactions at the cathode, is whether O_2 or HO_2 can bond to them . This can be evaluated by calculating the adsorption energy, E_{ads}, given by,[14]

$$E_{ads} = E(XY) - E(X) - E(Y) \qquad (5)$$

where X is N_2^-, N_4^- and N_8^- and Y is O_2 or HO_2. If the result is a negative value, it indicates O_2 or HO_2can form a stable bond with the radicals.

III RESULTS

Figure 1a and 1b show the optimized structures at minimum energy of N_8O^- and $N_8O_2^-$. The structures have no imaginary frequencies indicating they are at a minimum on the potential energy surface. The bond dissociation energy to remove an O atom from $N_8O_2^-$. Is calculated to be 4.67 eV slightly less than the calculated BDE to dissociate free O_2 which is 5.03 eV. Figure 2a and 2b illustrate the calculated minimum energy structure of $N_4O_2^-$ and N_4O^- which have no imaginary frequencies. The BDE calculated to remove an O atom from $N_4O_2^-$

is 4.08. Figure 3a and 3b show the optimized structures at minimum energy of $N_2O_2^-$ and N_2O^-. The calculated BDE to remove an O atom from $N_2O_2^-$ is 4.67 eV. These results indicate that $N_8O_2^-$, $N_4O_2^-$ and $N_4O_2^-$ would not be highly effective catalysts for O_2 dissociation as the BDEs are only slightly less than that needed to dissociate free O_2.

Figure 4 shows the optimized structure at minimum energy of $N_2O_2H^-$. The structure has no imaginary frequencies. The calculated BDE to remove an OH from it is 2.58 eV. Figure 5 shows the optimized structure at minimum energy of $N_4O_2H^-$ .The BDE to remove OH from it is calculated to be 0.49 eV. Figure 6 shows the optimized structure at minimum energy of $N_8O_2H^-$. This structure had no imaginary frequencies. The BDE to remove an OH from it was calculated to be 0.54 eV. which is much less than calculated BDE to remove OH from free HO_2 which is 5.79 eV. The calculated structure at minimum energy of HO_2 had no imaginary frequencies indicating it can exist as a free entity. Table I tabulates all the BDEs to remove an O atom from O_2 bonded to all the nitrogen radicals and to remove an OH from HO_2 bonded to the radicals.

Table II presents the calculated adsorption energy for O_2 and HO_2 to bond to all the nitrogen radicals considered, showing that because they are negative, a stable bonds can form. Interestingly, a calculation of E_{ads} for non paramagnetic molecules such as N_2, N_3^-, N_8^0 yield positive values suggesting that nitrogen radicals are necessary for potential catalysts. This is plausible in that the radical species have an available bond for the O_2 or HO_2 to bind with.

CONCLUSION

Density functions calculations of the structure at minimum energy of $N_2O_2^-$, N_2O^- ,$N_4O_2^-$, N_4O^- $N_8O_2^-$ and N_8O^- indicate the structures have no imaginary frequencies and are therefore at a minimum on the potential energy surface. The calculated bond dissociation energy to remove an O atom from, $N_2O_2^-$, $N_4O_2^-$, and $N_8O_2^-$ are only slightly less than that needed to dissociate free O_2 into two O atoms. This suggests that these molecules would not be highly effective catalysts for the molecular oxygen dissociation in fuel cells. However, the bond dissociation energy to remove OH from HO_2 bonded to N_4^- and N_8^- is considerably smaller than that needed to dissociate free HO_2 into O and OH. These nitrogen radicals are predicted to be effective catalysts for the HO_2 dissociation. Calculation of the adsorption energy for O_2 and HO_2 on all the radicals yield a negative values indicating they can bond with the radicals.
The results support the explanation for the recently observed catalytic effect of electrochemically deposited nitrogen radicals on carbon nanotube paper which were attributed to N_8^- but suggest the HO_2 reaction is being catalyzed.[7]

Table I Calculated bond dissociation energy to remove an O atom from O_2 bonded to the nitrogen radicals and OH from HO_2 bonded to the radicals.

REACTION	BOND DISSOCIATION ENERGY ,eV
$N_2O_2^- \rightarrow N_2O^- + O$	4.85
$N_4O_2^- \rightarrow N_4O^- + O$	4.08
$N_8O_2^- \rightarrow N_8O^- + O$	4.67
$N_2O_2H^- \rightarrow N_2O^- + OH$	2.58
$N_4O_2H^- \rightarrow N_4O^- + OH$	0.49
$N_8O_2H^- \rightarrow N_8O^- + OH$	0.54

Table II Calculated adsorption energies for O_2 and HO_2 on nitrogen radicals.

Radical	ADSORBED MOLECULE	E_{ads} (eV)
N_8^-	O_2	-0.32
N_4^-	O_2	-20.53
N_2^-	O_2	-9.80
N_8^-	HO_2	-1.33
N_4^-	HO_2	-22.07
N_2^-	HO_2	-3.04

Figures

1. (a) Calculated structure at minimum energy of O_2 bonded to N_8^- and (b) O bonded to N_8^- .
2. Calculated structure at minimum energy of (a) $N_4O_2^-$ and (b) N_4O^- .
3. Calculated structure at minimum energy of (a) $N_2O_2^-$ and (b) N_2O^- .
4. Calculated structure of at minimum energy of HO_2 bonded to N_2^-.
5. Calculated structure at minimum energy of $N_4O_2H^-$.
6. Calculated structure at minimum energy of O_2H bonded to N_8^- .

- coordinates of optimized structures will be provided on request.

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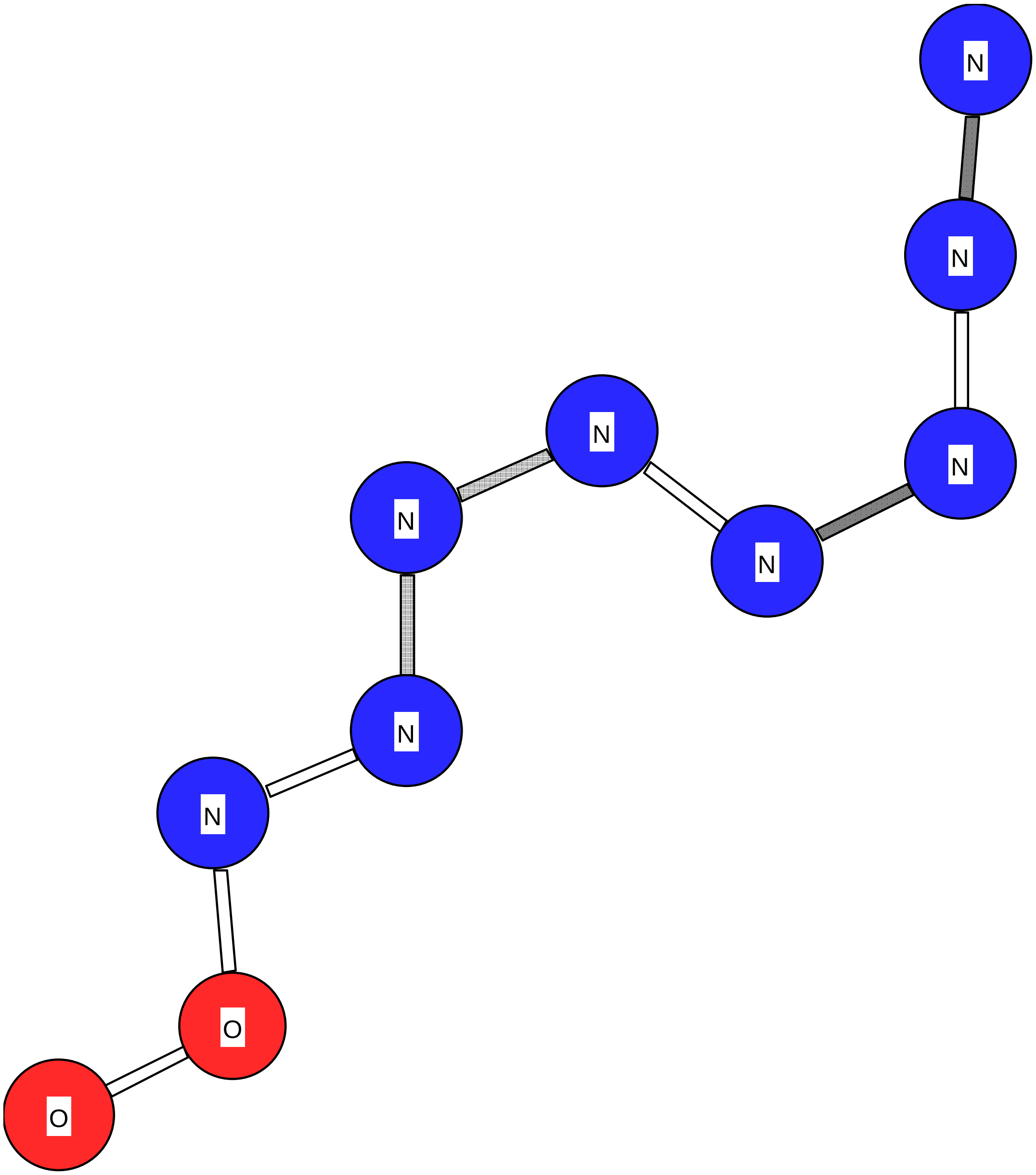

Fig. 1a

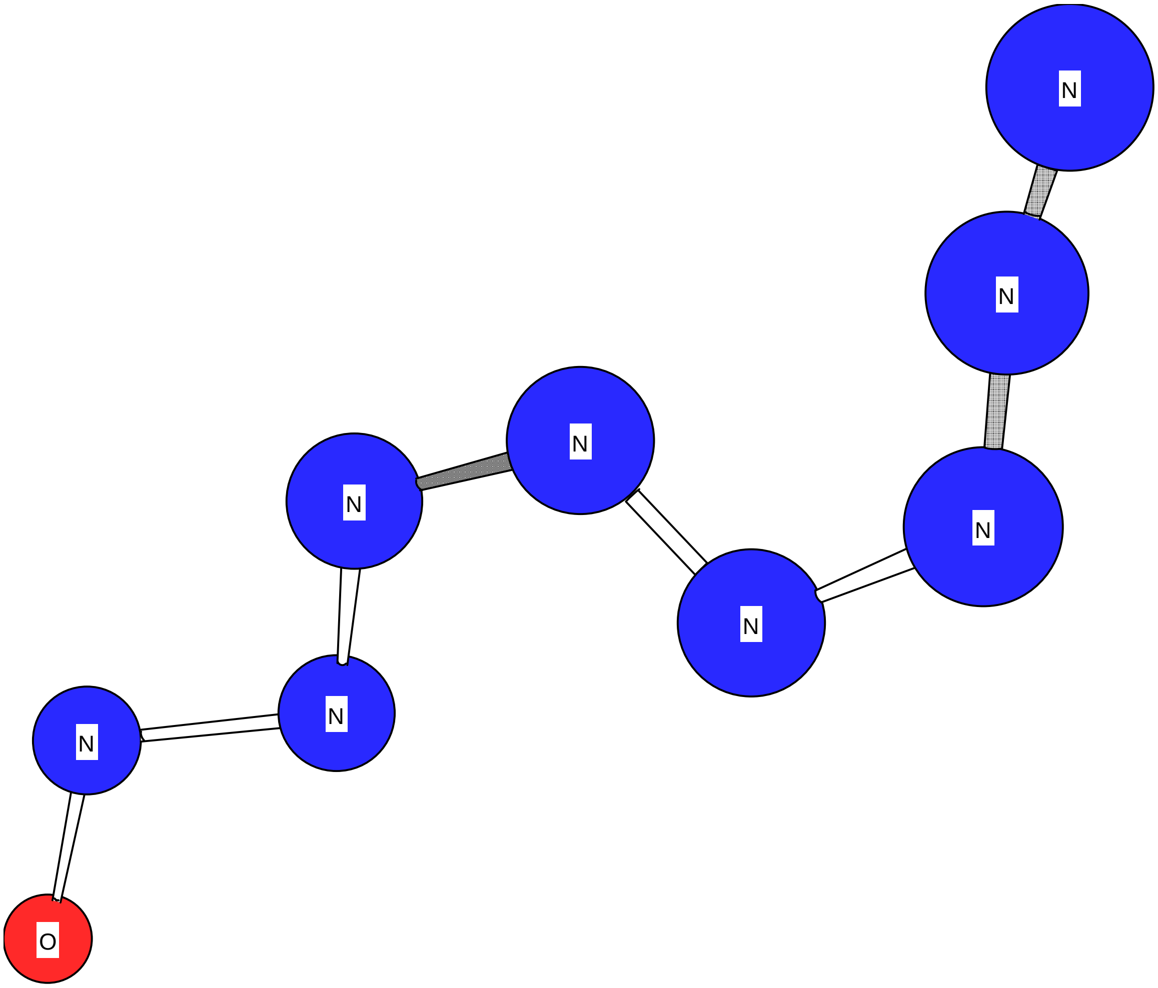

Fig. 1b

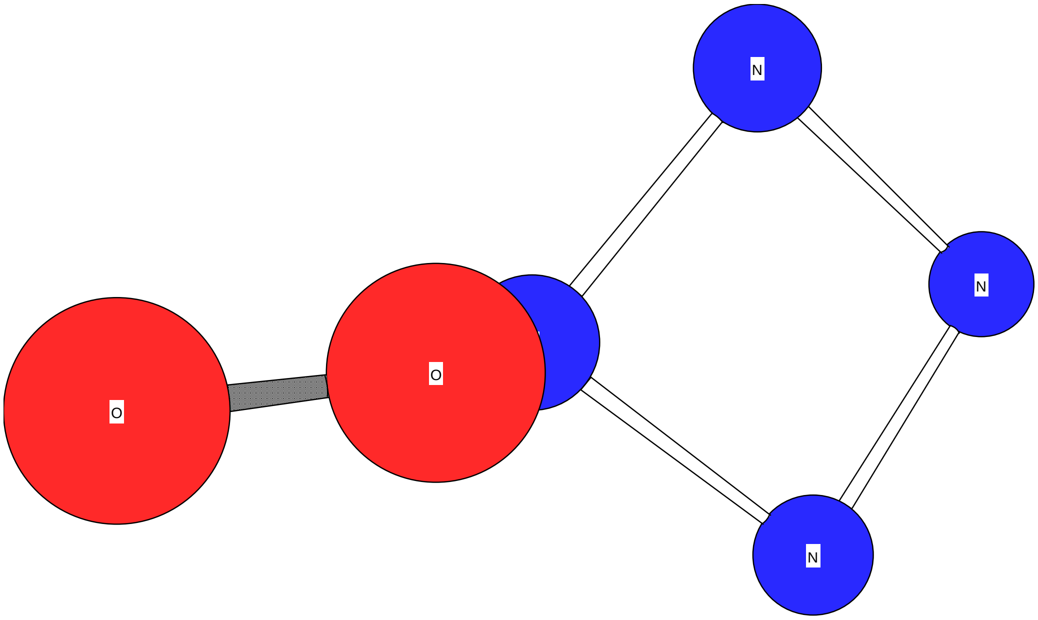

Fig. 2a

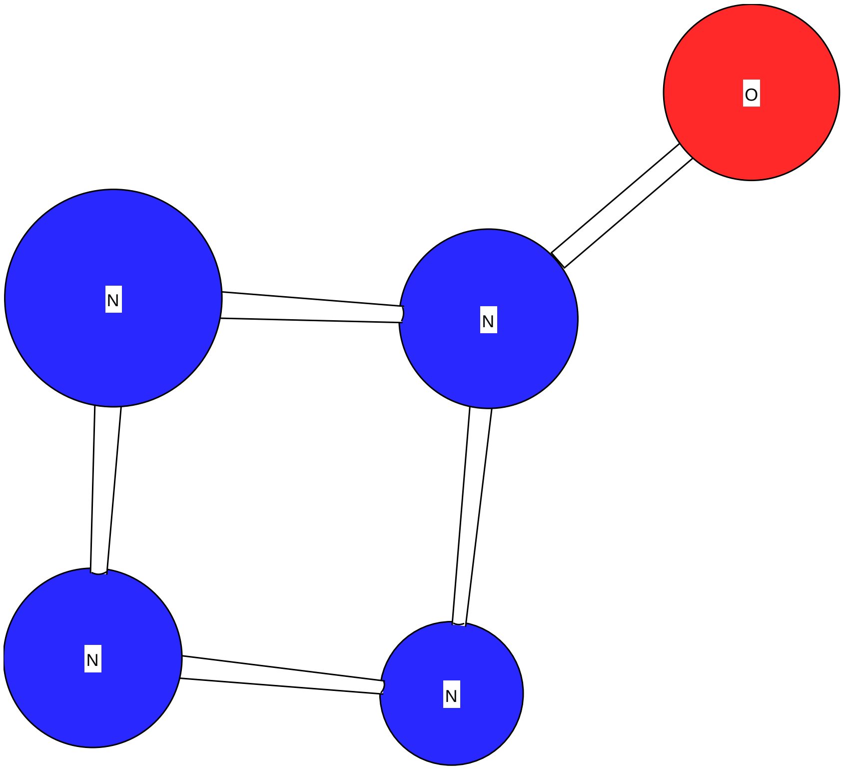

Figure 2b

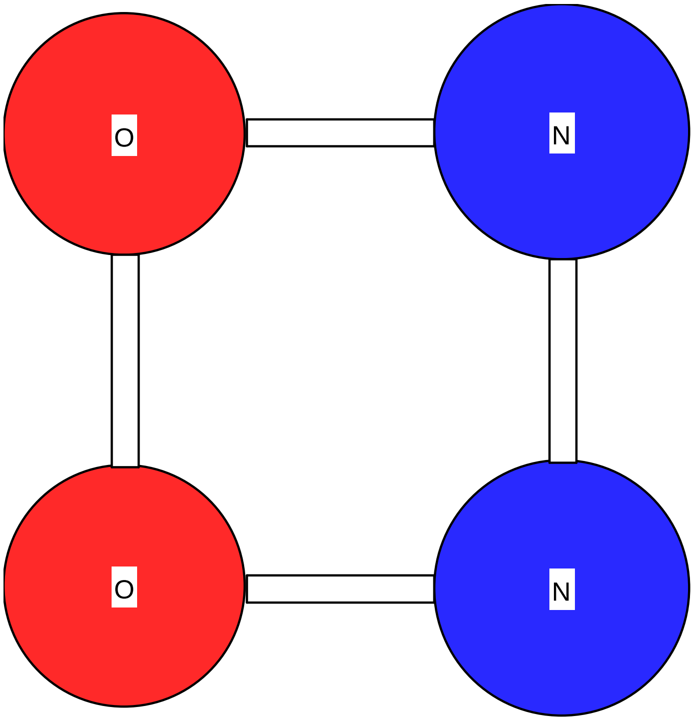

Fig. 3a

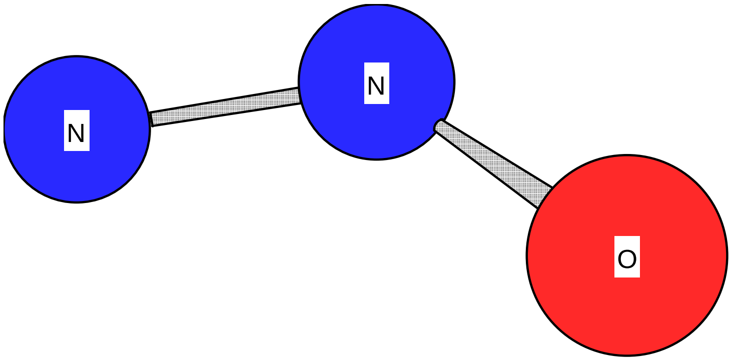

Fig. 3b

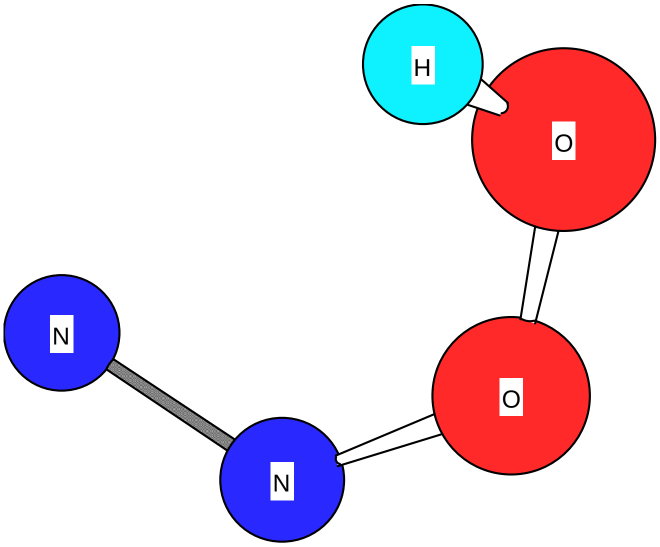

Fig. 4

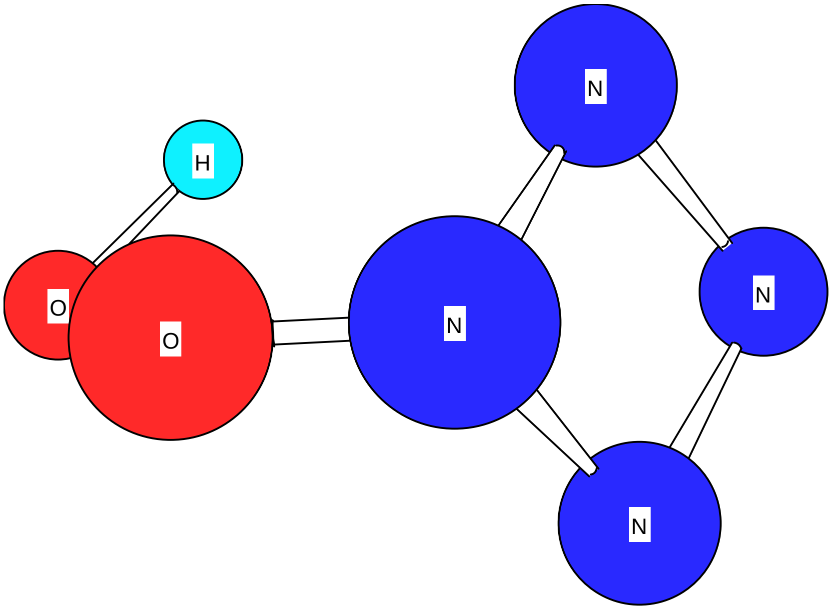

Fig. 5

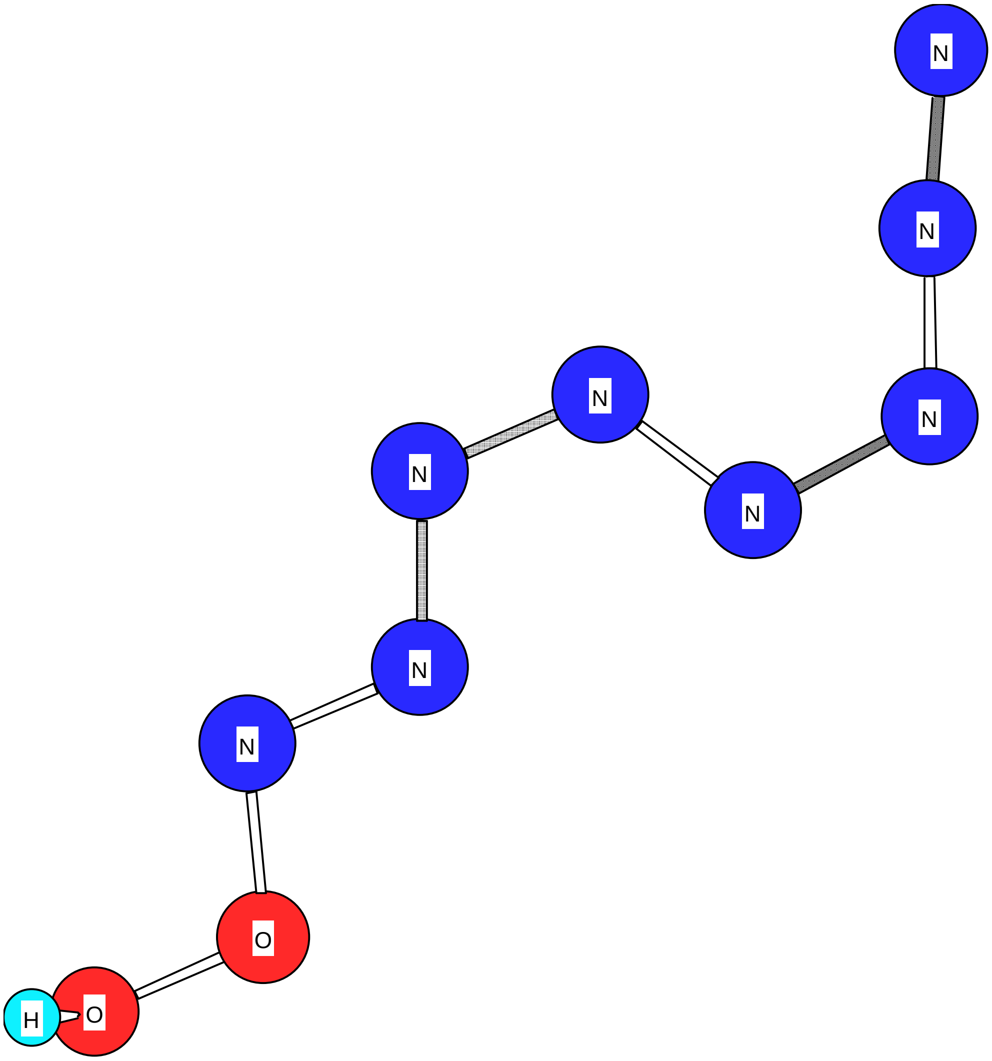

Fig. 6