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### Orientalional Effect of N<sub>2</sub> on Nitrogen Fixation

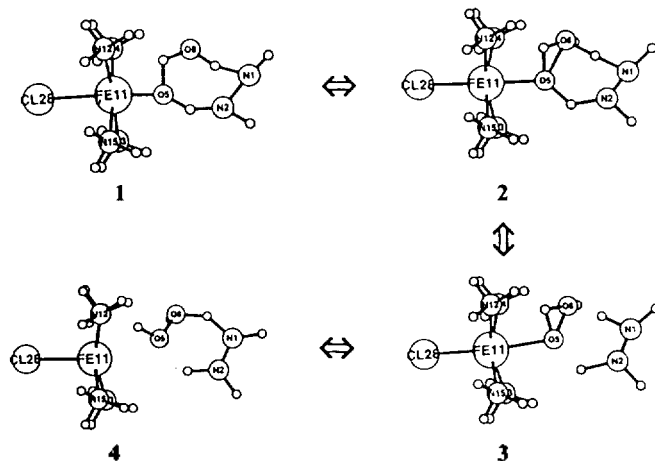
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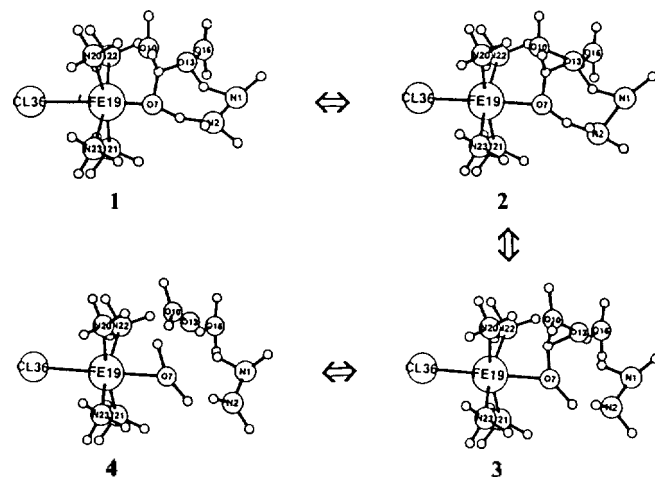
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We have reported the effect of water on nitrogen fixation, and tried to investigate the nitrogen reduction processes by inserting the water cluster. One atom of N<sub>2</sub> molecule participates in constructing the ring structure with waters and Fe-substrate discussed in our previous paper<sup>1</sup>. With such a model, the reduction mechanisms could be explained fairly well in some respects.

In this work, we tried to find out another possible process



**Figure 1.** Reduction processes to amine species with using 2H<sub>2</sub> O<sup>+</sup> during the INDO optimization. N<sub>2</sub> molecule is bonded to the intermediate water cluster as parallel (side-on bonding). Structure 1 is the starting model and others are intermediate structure obtained during the optimization. The electronic energy (in au) of each structure is -144.8158 for 1, -145.0508 for 2, -145.1660 for 3, and -145.6871 for 4.



**Figure 2.** Reduction processes to amine species with using 4H<sub>2</sub> O<sup>+</sup> during the INDO optimization. N<sub>2</sub> molecule is bonded to the intermediate water cluster as parallel (side-on bonding). Structure 1 is the starting model and others are intermediate structure obtained during the optimization. The electronic energy (in au) of each structure is -180.1048 for 1, -180.6503 for 2, -181.1508 for 3, and -181.4186 for 4.

on the basis of the previous work, and to concentrate our attention on directional effect of nitrogen molecule which approaches to the complex of water-substrate. Lots of tests were done with changing the orientation of nitrogen molecule perpendicular to that of the structure employed in the previous work. Actually, Fe-substrate not constructing the ring structure with water molecule repels the nitrogen molecule, and it doesn't show any reduction process. But, under the situation constructing the complex with water and Fe-substrate, we could observe the unexpected phenomena even though we varied the direction of N<sub>2</sub> to form a side-on bonding. At certain respects, similiar or more reasonable reduc-

tion processes than the previous work might be obtainable as shown in Figures 1 and 2. The molecular energy of each state depicted in Figures 1 and 2 is slightly lower than that of end-on bonding in the previous work.

By taking the reference models as the structure 1 in Figures 1 and 2, we carried out the same computational procedures as described in the previous paper<sup>1-4</sup>. In the model of end-on bonding being the electrons in N<sub>2</sub> inclined to Fe(II) of Fe-substrate, it is possible to form a bond between electron sufficient nitrogen atom and electron deficient Fe(II) atom of Fe-substrate. Only based on the end-on bonding, various schemes and processes were considered and discussed in the preceding work<sup>1</sup>. In the case of side-on bonding, the situation is quite different, because of difficulties to get the induced dipole due to the symmetric electrostatic fields. However, we can get the reasonable reduction process as in Figures 1 and 2 even though N<sub>2</sub> molecule was approaching in the direction perpendicular to that used in the previous work.

Under the condition of intermediate water structure made by Fe-substrate and water molecules, the role of intermediate water might be very important in reduction process<sup>5-6</sup>. The intermediate water structure makes structural changes as shown in Figures 1 and 2.

In fact, it is believed that the effective site of nitrogenase was constituted with the composition of MoFe<sub>6-8</sub>S<sub>8-9</sub>, and 4Fe-4S clusters were considered as the main active component of Fe-protein<sup>7-10</sup>. Being the active site quite large and symmetric as mentioned above, we can imagine that N<sub>2</sub> molecule captured at the active site might not be affected by its orientation.

As a result, the model of side-on bonding could also show the reasonable reduction process same as in the model of end-on bonding, and we can conclude that the reduction processes in nitrogen fixation are not affected by the orientation of N<sub>2</sub> molecule.

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## Facile Synthesis and Functionalizations of a Tetrakis(bromomethyl)cavitand

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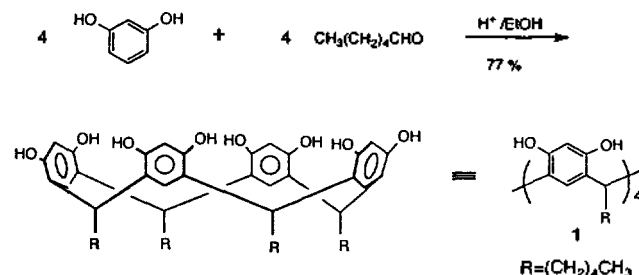
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The recognition study on a molecular level is the fundamental scientific object to understand the beginning of biological system. The interactions interested in molecular recognition are hydrogen-bonding force, hydrophobic, charge-charge, charge-dipole, and dipole-dipole interactions. These interactions are usually less than 10% of covalent forces and so very delicate to the structural and electronic complementarity between receptor (host) and substrate (guest).<sup>1</sup> Several of these interactions function cooperatively to maximize the recognition efficiency enough to sustain and evolve the biological systems.

Many artificial organic receptors have been developed as models for the study of various biological phenomena. Crown ethers<sup>2</sup>, cryptands<sup>3</sup>, spherands<sup>4</sup>, cyclophanes<sup>5</sup>, calixarenes<sup>6</sup>, cavitands<sup>7</sup>, carcerands<sup>8</sup>, hemicarcerands<sup>9</sup>, molecular clefts<sup>10</sup>, molecular tweezers<sup>11</sup>, and cyclodextrins<sup>12</sup> are among them. Cavitands are the compounds which have a defined cavity for substrate binding. They are being used as various hosts as well as important intermediates for carcerands and hemicarcerands, but only a few functionalized cavitands are reported.<sup>7,8</sup> In this paper we report the facile synthesis and multifunctionalization of tetrakis(bromomethyl)cavitand **8A**.

The acid-catalyzed condensations of resorcinols and aldehydes by the four fold oligomeric cyclization reaction (Scheme 1) give various conformationally stable octols (cyclo-tetramers) in high yields.<sup>13</sup> The easy syntheses and functionalizations of the bowl-shaped octols could provide potential sources of molecular vessels for the preparation of polyfunctional host systems whose convergent heteroatoms can act



**Scheme 1.**