

# Design of a New Nano Hinge Molecular Machine Based on Nitrogen Inversion: Computational Investigation

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**ABSTRACT:** *Ab initio calculations were employed to investigate nitrogen inversion as a configuration change that can supply an infinitely useful switchable control mechanism for some complex systems. In this paper, design of a new artificial molecular nanohinge is discussed based on nitrogen inversion in which reciprocating motion of substituent in effect of inversion phenomenon, led to an open–close motion in the molecule. Since the simple secondary amines easily face inversion process in the room temperature, a carboxamide derivative was selected as the initial driver for the molecular motion. The most critical finding from this study was that, following the displacement of the substituent attached to the amide nitrogen, making the xanthenes planar be dislocated and form hinge like reversible move.*

**KEY WORDS:** *Nanohinge; Configuration changes; Nitrogen inversion; Amide; Ab initio calculations.*

## INTRODUCTION

As a machine is a combination of different designed mechanism, every part is defined to serve a special purpose to improve the overall performance and therefore to transfer the energy with a higher quality.

This approach may also be applied to molecular indicator in nanoscale. To achieve this, some molecular elements must be set in a special manner to serve the set purposes and perform motor–like movements, directional turns, etc [1]. Research, design and production of nanomachines, which can be used in the world of chemistry, are not only of interest in basic and pure research, but also in the growth and development of

nanotechnology and its related research studies [2,3]. A nanomachine, is a mechanical or electromechanical device whose dimensions are measured in nanometers (millionths of a millimeter, or units of  $10^{-9}$  meter). Nanomachines are largely in the research-and-development phase, but some primitive devices have been tested. An example is a sensor having a switch approximately 1.5 nanometers across, capable of counting specific molecules in a chemical sample. The first useful applications of nanomachines will likely be in medical technology, where they could be used to identify pathogens and toxins from samples of body fluid.

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Fig 1: Nitrogen inversion.

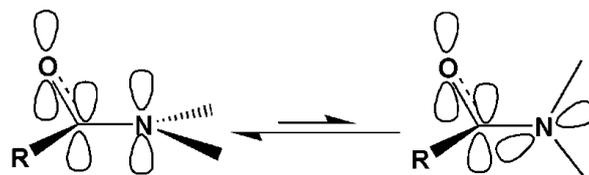


Fig 2: N-inversion in Amides with low speed due to high rotation barrier

Another potential application is the detection of toxic chemicals, and the measurement of their concentrations, in the environment.

The technology of nanomachinery that creates machines or robots in the scale of nanometer can also called nanorobotic [4-6]. More specifically, nanorobotics refers to the nanotechnology engineering discipline of designing and building nanorobots which move and do specific work. Therefore, a nanomachine or molecular machine can be defined as a group of distinct nanoscale molecular combinations. So it can be said that a molecular machine is a set of compound molecules and each can change in specific locations due to external stimulus. Though nature provides living structures with a large number of molecular machines and motors with high standard structures and complicated functions, chemists are more interested in developing and progressing simpler sets which are entirely synthetic [7].

Controlling molecular movements is an important stage of advancing and manufacturing machines and parts in molecular scale. A great deal of research has been carried out regarding the control of molecular turns and shuttle-like process based on different processes which can be used to create small primary movements and consequently transferring such small movements to the other parts of molecule and thus create more diverse and objective movements. Configurational change is one of such movements with a small domain which can be used to design the molecular machines [8]. Although this small amplitude motion is not generally sufficient for direct exploitation as a machine, it can supply an infinitely

useful switchable control mechanism for more complex systems. Much of the recent published research has been directed at exploiting a configuration change, such as N=N bond in azocompounds, but very little effort has thus far been put towards using the lever like motion of nitrogen pyramidal inversion. Nitrogen pyramidal inversion is derived from changing nitrogen's substituents position and can exist in two distinct geometric configurations (Fig. 1). These configurations are interchangeable by transposition of the substituents to the opposite side of the central atom, thereby formation a mirror image of the original molecule [9-14].

As the inversion speed of nitrogen in simple secondary amines without pressure is very high and the inversion may even take place in the room temperature, these amines may be unsuitable to serve as stimulus to make a molecular machine movement. This is due to the difficulty of controlling the movements and also the difficulty of separating the produced conformers.

So for obtaining compounds with controlled range of movements, it is necessary to use nitrogen compounds which are not turned (converted) to secondary conformers easily. Amide is one of the compounds which experiences nitrogen inversion at a lower speed. This is due to amides prefer planar geometry because of the resonance stabilization. The barrier to rotation is associated with the disruption of this resonance. In MO terminology, the orbital with the C=O  $\pi^*$  orbital provides a stabilized delocalized orbital. The non-planar form leads to isolation of the nitrogen unshared pair from the C=O system [15] (Fig. 2).

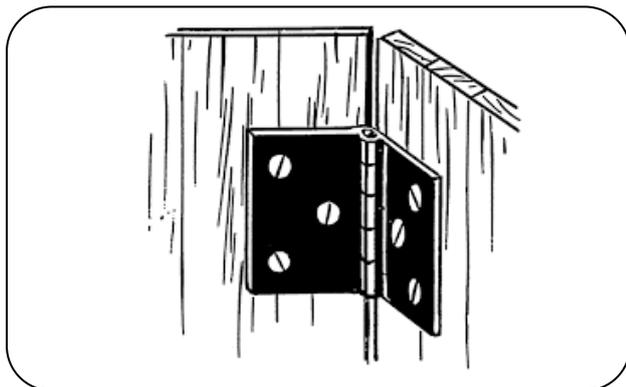


Fig 3: Schematic representation of a hinge.

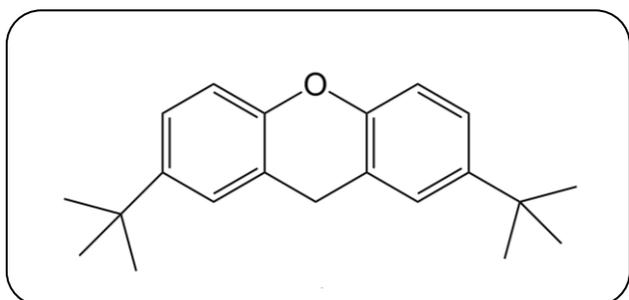


Fig 4: Xanthene unit.

A nanohinge is an important molecular device that can be used alone or as a part of a complex system toward special purposes. Based on the above-mentioned explanations, in this work, the design of a new molecular hinge is introduced, in which amide nitrogen inversion was used to start-up the motion in the hinge-like molecular machine.

#### COMPUTATIONAL METHODS

Geometry optimizations were performed at B3LYP/6-311G (d,p) level of theory without any symmetry constraint and all the calculations were carried out using a locally modified version of the GAMESS electronic structure program [16].

#### RESULTS AND DISCUSSION

Hinge or joint is a tool for connecting two parts in such a manner that one or both parts could rotate around the axis of the hinge to some degree. There are many different kinds of hinges used in different instruments and machines. The most common type is the one that is installed in doors and windows. Some joints in animal bodies function as hinges do. (Fig. 3)

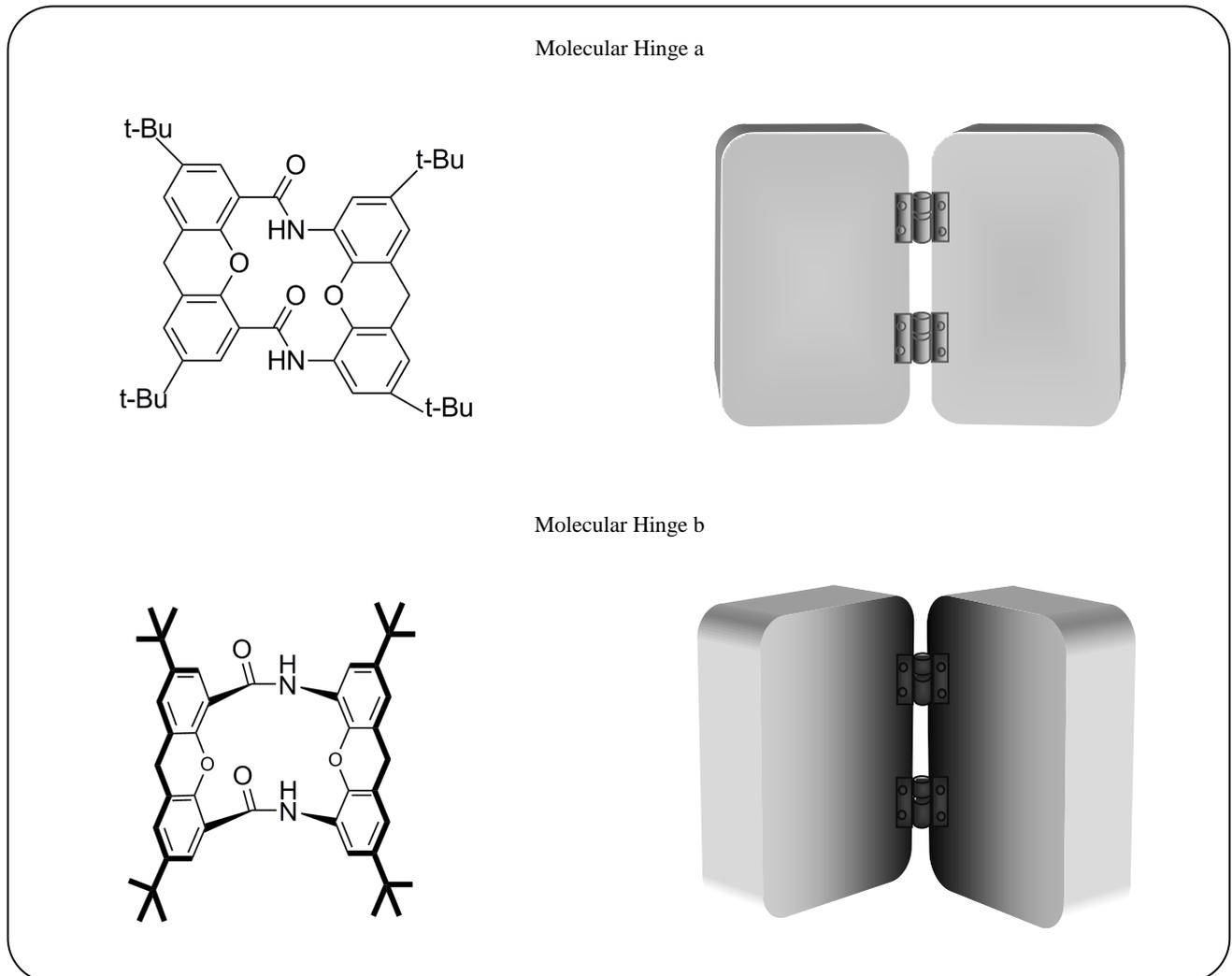
Inspired by the form of common hinges, it was decided to design a hinge-like molecular machine in molecular size with the ability to move back and forth using the power created by nitrogen inversion. It should be noted that in this design, the nitrogen inversion present in carboxamide was used as initial stimulus power to activate the molecular machine. The selected molecules must be appropriate to serve as hinge planar. Two units of xanthenes seemed to offer the best choice. (Fig. 4)

Xanthene is a suitable compound with the ability to retain its planar form in both folded and unfolded forms of a hinge.

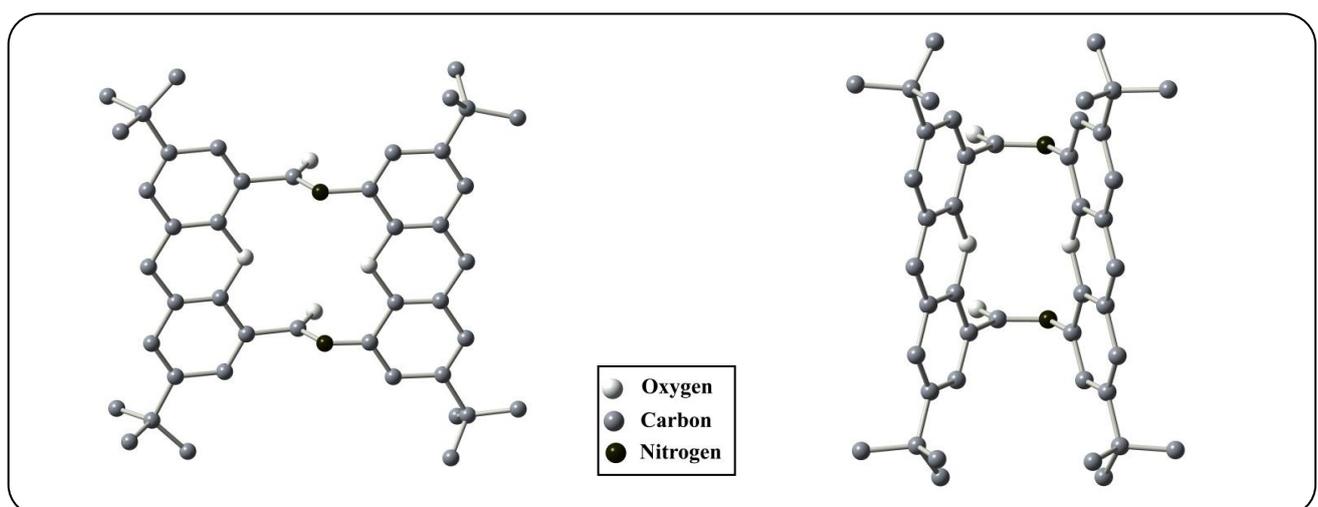
At this stage, carboxamide was considered to act as the axis of this molecular hinge. This introduced a better quality of control on the back and forth moves created by the inversion. Finally, after considering features, the molecular hinge was designed as illustrated below.

Fig. 5 demonstrates that nitrogen inversion presented in amide part of this molecular set altered the location of xanthenes planar which was on nitrogen atom. At the stage of inversion, this planar which was attached to nitrogens folded and unfolded just like a hinge.

As it can be observed, the existing nitrogen inversion in carboxamide attached to the xanthene units created an open-close motion for this new molecular hinge and caused the two planar units to be close and far from each other. Evaluation of the energy data obtained from the ab initio calculation using the Hartree-Fock as the method and 6-311G\*\* as the basis set showed that (a) conformation was about 8.35 kcal/mol more stable than (b) conformation. As can be seen in Fig. 6, in the (b) conformation, due to approaching the planar units, a repulsive force was generated in several parts of the molecule, resulting in less stability of (b) conformation than (a) conformation. The structural information obtained from the ab initio calculation using the Hartree-Fock as the method and 6-311G\*\* and comparison of the dihedral angles (C-C-C-C) between the hinge and planar units in the optimized conformations of the molecular hinge showed that the dihedral angles in (a) conformation in Fig. 6 changed from  $-172.17^\circ$  to  $-3.98^\circ$  in (b) conformation (Table 1). These results made it clear that utilizing nitrogen inversion could establish angle changes that caused the attached planar units to nitrogens folded and unfolded just like a hinge.



**Fig. 5:** Open-close motion of the molecular hinge based on N-inversion in carboxamide (left), schematic representation of open-close motion of the molecular hinge. The hinge are shown in yellow.



**Fig. 6:** The dihedral angle between the hinge and planar units of the hinge molecular machine.

**Table 1: Energy differences ( $\Delta E$ ), and the dihedral angles between the (C-C-C-C) hinge and planar units of the hinge molecular machine.**

structure	$\Delta E$ (kcal/mol)	C-C-C-C (Degree)
a	0.00	-172.17
b	8.35	-3.98

Since a nanohinge is an important molecular device that can be used alone or as a part of a complex system toward special purpose, the design of a new nanohinge was introduced based on nitrogen inversion. As it can be noticed in the calculations, nitrogen inversion can be used as the initial motion to establish more diverse moves in a series of joined molecules. The connection of amide units as the hinges to xanthenes units as the planar form a molecular hinge which performed an open-close motion and proved that nitrogen inversion in amid compound of this molecular set could put the hinge like molecular machine in motion. Configurational changes of substitution attached to two amidic nitrogens make xanthenes planar be dislocated and form hinge like reversible move. Generally, this study showed that by exploiting specific molecules that can perform specific movements as initial motion, a series of molecules can be joined as a molecular machine or robot that can do significant tasks and may be useful for next investigation.

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