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COMPUTATIONAL DESIGN OF A NEW PEDAL-LIKE NANOROBOT BASED ON NITROGEN INVERSION

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Ab initio calculations are 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, the design of a new pedal-like nano-scale robot is discussed based on nitrogen inversion. This work introduces the design of a nano pedal in which different structures of the arms created two diverse kinds of pedals: a) nano pedal without intersectional motion and b) nano pedal with intersectional motion. In (*a*), due to stereo repellent in the two pedal arms, they were unable to pass each other and could only move back and forth in one direction. However, in (*b*), due to an increase in the axis connecting the two arms, the issue of stereo repellent of nitrogen was looked over and the arms could pass each other and moved in a larger domain.

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K e y w o r d s: nanorobot, nano pedal, nitrogen inversion, *ab initio* computation.

INTRODUCTION

Most of the achievements and developments, regarding the standard of human life and the ability to improve production power, have originated from the invention of different kinds of machines and their related parts and consequently their technological advancement. In the past, this issue was concentrated mainly on mechanical machines, but at present the most noticeable progress is related to the invention and promotion of computer-controlled electronic machines and parts, i.e. computerized ones [1].

Since a robot or a machine is a combination of different designed mechanism, each 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 can also be applied to a molecular indicator. To achieve this, some molecular elements must be set in a special manner to serve the set purposes and work as a nanorobot or a nanomachine.

The field creating robots or machines whose components are at or close to the scale of nanometer (10^{-9} meters) is called nanorobotics [2—4] that refers to the nanotechnology engineering discipline of designing and building nanorobots. A nanorobot can be defined as a molecular machine consisting of a group of distinct molecular combinations. Therefore, it can be said that a nanomachine is a set of compound molecules and each can change in specific locations due to external stimulus. Nanomachines are largely in the research-and-development phase [5], but some primitive molecular machines and nanomotors 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 might be in medical technology [6, 7], which could be used to identify and destroy cancer cells [8, 9]. Another potential application is the detection of toxic chemicals, and the measurement of their concentrations in the environment. Indeed, the fabrication of simple nanorobots can be used to create more complex systems. Although nature provides living structures with a large number of molecular machines with high standard structures and complicated functions, chemists are more interested in developing and progressing simpler sets which are entirely synthetic [10].

The control of molecular movements is an important stage of advancing and manufacturing machines and parts in the molecular scale. So far a great deal of research has been carried out regarding the control of molecular turns and shuttle-like movement based on different processes [11]. There are cases which can be used to create small primary movements and consequently transferring such small movements to the other parts of the molecule and thus create more diverse and objective movements [12]. A configurational change is one of such movements with a small domain, which can be used to design the molecular machines [13]. Nitrogen inversion is a configurational change and very few studies have reported the control of the moves in the molecular machines based on it. Since the inversion speed of nitrogen in simple secondary amines without pressure is very high, and the inversion may even take place at room temperature, these amines are 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. Thus, to obtain compounds with a controlled range of movements, it is necessary to use nitrogen compounds which are not easily turned (converted) to secondary conformers [14].

Aziridine is one of the compounds experiencing nitrogen inversion at a lower speed. Nitrogen has a high energy barrier in aziridine, but of course, when considering the substitution related to the control of nitrogen, this barrier can change. An increase in the energy barrier causes the transfer motion of isomers to take place at a lower speed, so it leads to a more precise control of molecular moves of aziridine. Nitrogen inversion in aziridine and, more generally, amines can be conducted by supplying energy; needless to point that simple secondary amines easily face inversion process at room temperature Fig. 1. Considering the amine type, its situation in the compound, its presence in a high pressure ring, and the type of substituents connected to central nitrogen, the level of energy which is used to complete the inversion process is modified [15].

RESULTS AND DISCUSSION

Generally, in this paper the design of two kinds of a molecular pedal, based on configurational changes caused by nitrogen inversion in aziridine, is raised and investigated using computational methods. The *ab initio* computations were carried out using the Hartree—Fock method with the 6-311G** basis set [16]. All calculations were performed using the Gaussian 09 software.

Design of a molecular pedal based on nitrogen inversion in aziridine. In the world of microscopy, the pedal is an instrument formed by two identical parts with the ability to move in opposite directions. Some levers transfer the stimulus power identically to both parts (Fig. 2). The pedal can be used in several parts of a mechanical machine such as a boat to move it up and down.

Design of a molecular pedal with the ability to move non-intersectionally. Being inspired by the general form of a pedal, it was decided to design a molecular machine in the pedal form of a molecular size. To achieve this task, a molecule which could act as a simple lever was used to start setting the machine in motion. Therefore, the aziridine molecule in which the substituents undergo configurational changes due to nitrogen inversion was selected as the initial stimulus for operating the molecular machine.

In continuation of the study, new compounds were suggested for other parts of the pedal-like molecular machine. Since biphenyl has the ability to make a 360° turn round the axis connecting two groups of aromatics, it is considered to be a good applicant for the use as a hinge-like axis. In this compound, in a normal situation, the two phenyl groups are located with an angle of about 5° between them, but in specific cases, such as when power is applied, the phenyl groups fully turn round their connecting axis, i.e. 360° (Fig. 3).

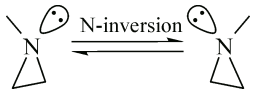


Fig. 1. N-inversion in aziridine

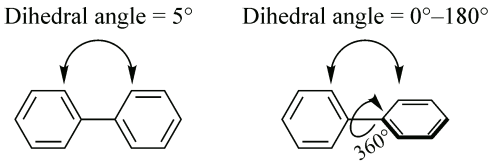
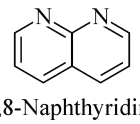


Fig. 3. Biphenyl 360° rotation around the connecting hinge



1,8-Naphthyridine

Fig. 4. The compound performing the pedal-like move

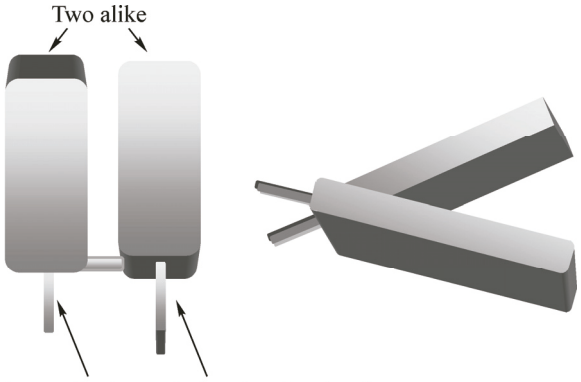


Fig. 2. Schematic representation of different parts of a pedal-like device from the front and the side

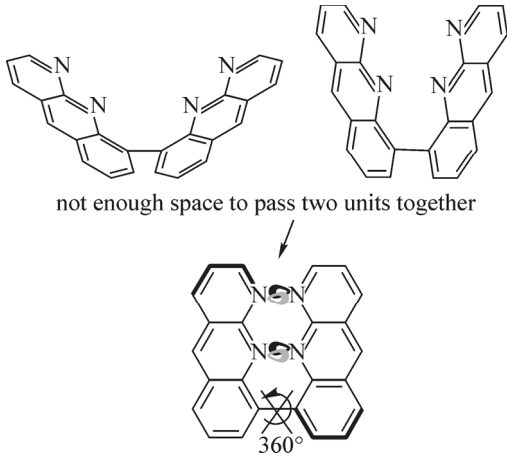


Fig. 5. Two units of 1,8-naphtiridine connected to the biphenyl unit

For the two parts which perform the pedal-like move, two units of 1,8-naphtiridine were applied (Fig. 4).

In the design of the molecular pedal, the two parts will not be able to pass each other well if the distance between the two units of 1,8-naphtiridine is satisfactory. This is due to the existence of stereo repellent against the nitrogen lone pair in the rings. Thus, these two pedal-like parts only have back and forth moves, but they do not pass each other. Since biphenyl is used as the required moving hinge, this distance equals the distance of a single bond which appears between two phenyl groups. Thus created distance is not enough for the two pedal parts to pass each other (Fig. 5).

Eventually it was decided to have these two units of 1,8-naphtiridine attached to biphenyl as molecular machine pedals, to have biphenyl as a hinge, and to have two units of aziridine attached to biphenyl as the levers to apply the power. These aziridine groups are connected to each other with a line having two units of CH_2 and also one unit of thiophen placed in the middle. This application will prevent the hinge from rotation (Fig. 6).

As observed in Fig. 6, the two 1,8-naphtiridine parts have a pedal-like motion, moving back and forth, but being unable to pass each other. The two aziridine moieties used in this molecular pedal from the very beginning have been enantiomers toward each other. Therefore, while applying energy and with the occurrence of the inversion phenomena, the substituents attached to aziridine units move in two opposite directions making the two phenyl rings in molecular hinges move in their opposite directions. This led to the pedal-like motion in the molecular machine. The evaluation of the energy

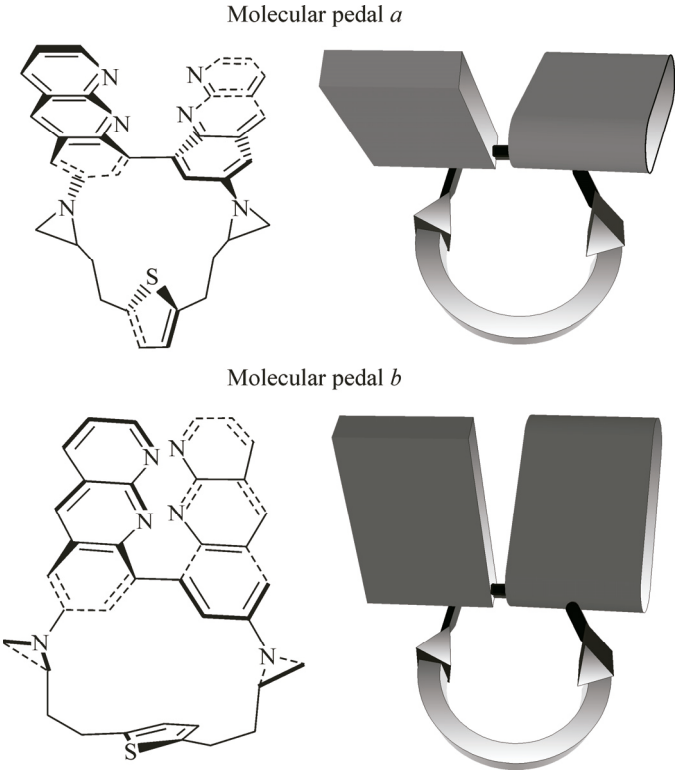


Fig. 6. Non-intersecting moves in a non-intersectional molecular pedal

T a b l e 1

Molecular energies (*E*), *energy differences* (Δ*E*), *and the dihedral angles between the two arms of non-intersectional molecular pedal*

Structure	*E*, Hartree	*E*, kcal/mol	Δ*E*, kcal/mol	C—C—C—C
a	–2104.0494389	–1320291.02	9.8	–123.18
b	–2104.0649873	–1320300.78	0.00	–61.55

data obtained from the *ab initio* calculation showed that (*b*) conformation was more stable than (*a*) conformation by about 9.8 kcal/mol. The structural information obtained from the *ab initio* calculation and the comparison the dihedral angles (C—C—C—C) between two phenyl groups of biphenyl in the optimized conformations of the molecular pedal showed that the bite angle between the molecular pedal arms in its open form was –123.18° and –61.55° in the close form (Table 1).

Design of a molecular pedal with the ability of intersecting moves. At the previous stage, the designed molecular pedals have the ability to move pedal-like but not intersecting with each other. This means that the two molecular pedal arms are not able to pass each other due to the existence of stereo hindrance against the nitrogen lone pair in their compounds. Thus, it was decided for a molecular pedal to be designed in such a way that its two arms could transfer intersectional moves caused by nitrogen inversion in aziridine to hinge part and then consequently to the two pedal-like parts. To fulfill the mentioned approach, a desired distance was required to allow the two pedal arms to pass each other. This could be achieved by increasing the distance between the two aromatic rings of the hinge connecting the two arms. To increase this distance, one unit of acetylene was located in between two biphenyl rings of the hinge to enable the arms to pass each other (Figs. 7, 8).

Since the distance between the two phenyl rings in the molecular hinge increased, the distance between the aziridine moieties was also increased but they could be connected by a longer line having

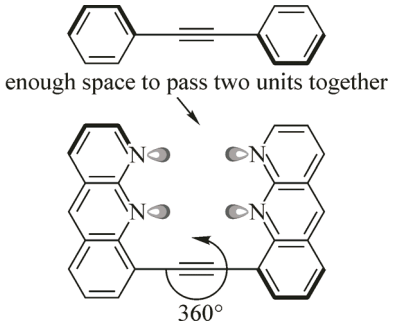


Fig. 7. Locating an acetylene unit between two phenyl groups of biphenyl

two CH_2 units and one biphenyl. As shown, the two arms then could freely pass each other and performed a complete pedal-like move (Fig. 8).

The evaluation of the energy data obtained from the *ab initio* calculation showed that (*a*′) conformation was more stable than (*b*′) conformation by about 5.7 kcal/mol. The structural information obtained from the *ab initio* calculation and the comparison the dihedral angles (C—C—C—C) between two phenyl groups of biphenyl in the optimized conformations of the molecular pedal showed that the bite angle between the molecular pedal arms changed from 76.70° to –120.68° (Table 2).

CONCLUSIONS

As observed in the calculations, nitrogen inversion may be applied as the initial move to establish more extended moves in a series of joint molecules. In this work, the design of a new pedal-like

T a b l e 2

Molecular energies (*E*), *energy differences* (Δ*E*), *and the dihedral angles between the two arms of the intersectional molecular pedal*

Structure	*E*, Hartree	*E*, kcal/mol	Δ*E*, kcal/mol	C—C—C—C
a′	–2088.7618224	–1310698.04	0.00	76.70
b′	–2088.7534143	–1310692.77	5.27	–120.68

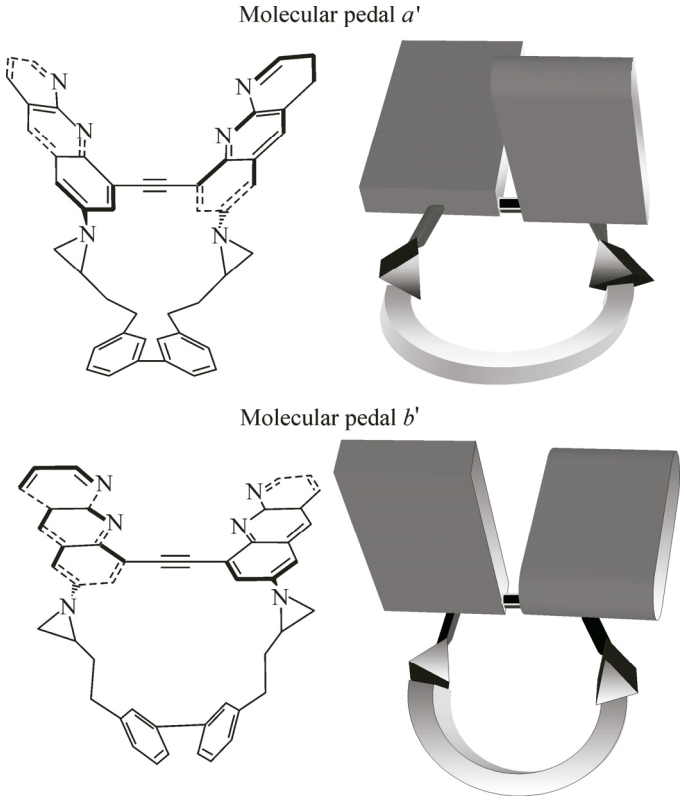


Fig. 8. Intersecting moves in the intersectional molecular pedal

nanomachine was introduced with the arms creating two different kinds of pedals: a) molecular pedal without intersectional motion and b) molecular pedal with intersectional move. In (*a*), due to stereo repellent in the two pedal arms, they were unable to pass each other and could only move back and forth in one direction. But in (*b*), due to an increase in the axis connecting the two arms, by using acetylene in between the two phenyl rings of the axis, the issue of stereo repellent of nitrogen was looked over and arms could pass each other and so moved in a larger domain.

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