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DESIGN OF A NEW ROTARY MOLECULAR MACHINE BASED ON NITROGEN INVERSION: A DFT INVESTIGATION

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Ab initio calculations are employed to investigate nitrogen inversion as a configuration change that can supply an extremely useful switchable control mechanism for some complex systems. In this paper, the design of a new artificial rotary molecular machine based on nitrogen inversion is discussed. The introduced design of a molecular rotator is based on the reciprocating motion of a substituent due to the inversion phenomenon, leading to the rotary motion in the molecule. Since simple secondary amines easily face the inversion process at room temperature, aziridine is selected as the initial driver for the molecular motion. The most obvious finding from this study is that, following the displacement of the substituent attached to the aziridine nitrogen atom, two rotary motions occurr in the molecule, one clockwise and another counterclockwise with a 39.52 to 150.09° angle domain.

INTRODUCTION

At the macroscopic level of living the most developments in the improvement of technology and productivity have originated directly from the invention of new functional devices and then the construction of novel machines. A device is something created for a specific purpose, whereas a machine is a combination of several devices to utilize, modify, apply or transmit energy [1]. This explanation can also be applied at the molecular level. For achieving this objective, it is necessary to properly arrange some molecular components to develop a system that can do useful work such as the directional rotation or shuttle-like movements [2]. Miniaturization is an essential issue in modern technology. In the recent fifty years, miniaturization in the employed components in the construction of devices and machines has led to dramatic gains in the technology, especially, in the field of information processing [3]. Since the concept of a device or machine in the macroscopic scale can be generalized to the molecular level, a molecular machine can be defined as an assembly of distinct molecular combinations. Therefore, a molecular machine is a multi-molecular complex in which each molecule can be changed to a specific state under an external stimulus [4]. Whereas the living structures in nature are full of molecular motors and machines with complex constructions and advanced functions, chemists are interested in the improvement of artificial simple molecular assemblies [5].

The design of molecular devices and machines based on the movement related to configuration changes and the subsequent interlocking motion in a molecular system is a significant step in the syn-
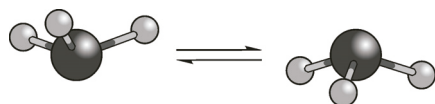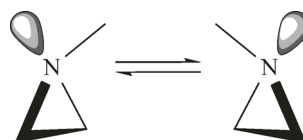
Fig. 1. Nitrogen inversion

Fig. 2. N-inversion in aziridine

thesis and improvement of devices and machines in the molecular scale [6]. Much of the recent published research has been directed at exploiting a configuration change, such as the N=N bond in azo-compounds, but very little effort has thus far been put towards using the lever-like motion of nitrogen pyramidal inversion. Nitrogen pyramidal inversion is induced by changes in the of position nitrogen substituents and can exists in two distinct geometric configurations (Fig. 1). These configurations are interchangeable by the transposition of substituents to the opposite side of the central atom, thereby the formation of a mirror image of the original molecule [7—10].

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 can be unsuitable to serve as a 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, in order 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. Aziridine is one of the compounds which experiences nitrogen inversion at a lower speed (Fig. 2).

Nitrogen has a high energy barrier in aziridine, but of course, considering the substitution to control nitrogen, this barrier can be changed. An increase in the energy barrier causes the transfer motion of isomers to take place at a lower speed, therefore it enables a more precise control of aziridine molecular movements. Nitrogen inversion in aziridine and, more generally, amines can be conducted by supplying energy. Needless to point that simple secondary amines easily face the inversion process at room temperature. Considering the amine type, the situation in the compound, its presence in a high pressure ring, and the type of substitutions connected to the central nitrogen atom, the energy level used to complete the inversion process is modified [11—13].

Based on the above-mentioned explanations, in this work, the design of a molecular rotator was introduced, in which aziridine nitrogen inversion was used to start up the motion in the rotatory molecular machine.

RESULTS AND DISCUSSION

Generally speaking, any instrument can be called rotary if it has an axis and several wings attached to it, and when the external power such as electricity, wind, or mechanical power is applied, the wings start rotating about their axis. Rotary machines come in two different kinds: a) bidirectional machines with wings rotating both clockwise and counterclockwise; b) unidirectional machines with wings rotating either clockwise or counterclockwise.

Considering the form of a common rotary machine, it was decided to design a rotary in the size and extension of a molecule. This would rotate after applying the power created by nitrogen inversion. Thus, the chosen molecules which must stand as the axis and the attached wings were of great importance (Fig. 3). Bicyclo[2,2,2]octane was selected as the axis to serve the mentioned purpose. Two thiophene units attached to each of three aziridine groups were chosen as the required wings (Fig. 4).

Hence, the molecular rotary consists of one bicycle[2,2,2]octane unit as the axis, three aziridine units as the initial starter for the moves, and six thiophene units attached to aziridene as the wings (Fig. 5).
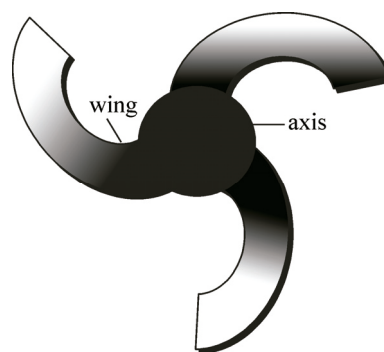

Fig. 3. Schematic representation of different parts of a rotator

a

Bicyclo[2.2.2]octane

b

Thiophene

c

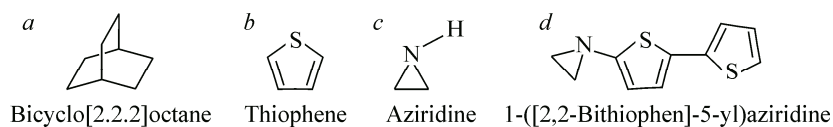Aziridine

d

1-([2,2-Bithiophen]-5-yl)aziridine

Fig. 4. Representation of different compounds used in several parts of the molecular rotator. Bicycle[2,2,2]octane as the axis (*a*), thiophene unit (*b*), aziridine unit (*c*), two thiophene units attached to each of three aziridine groups as the required wings (*d*)
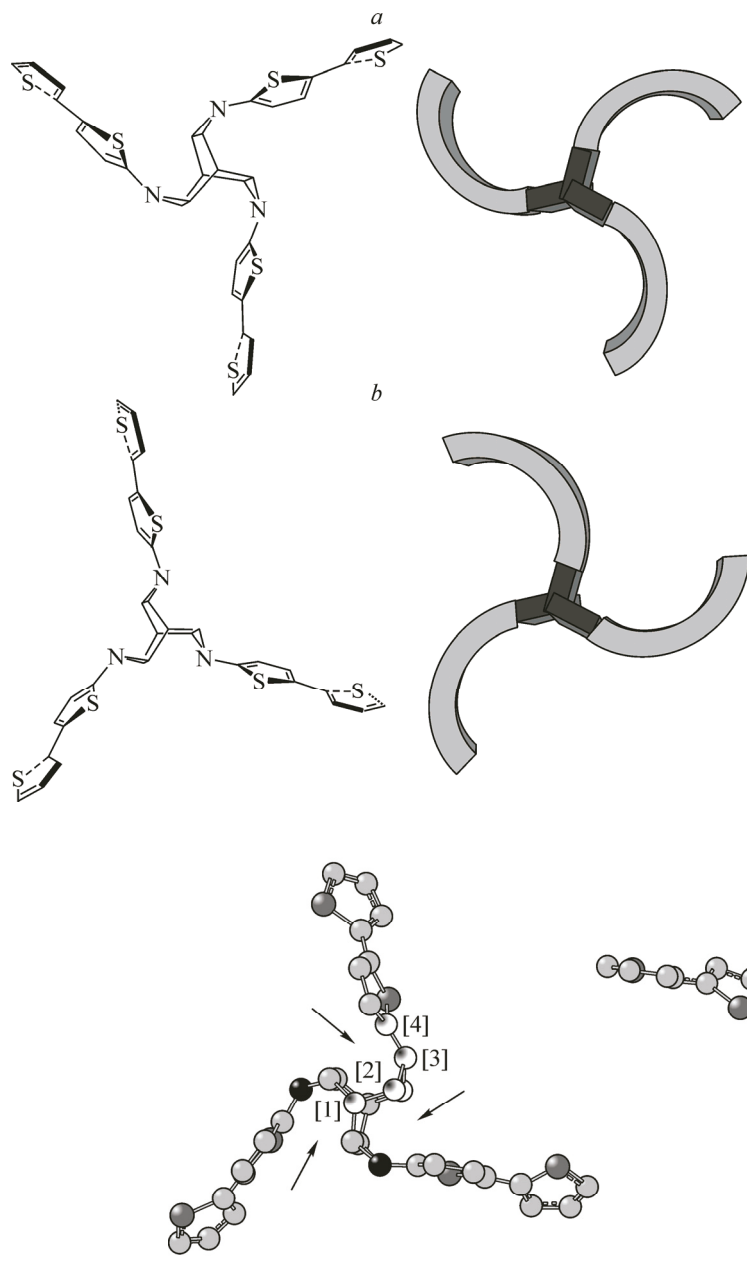
a

b

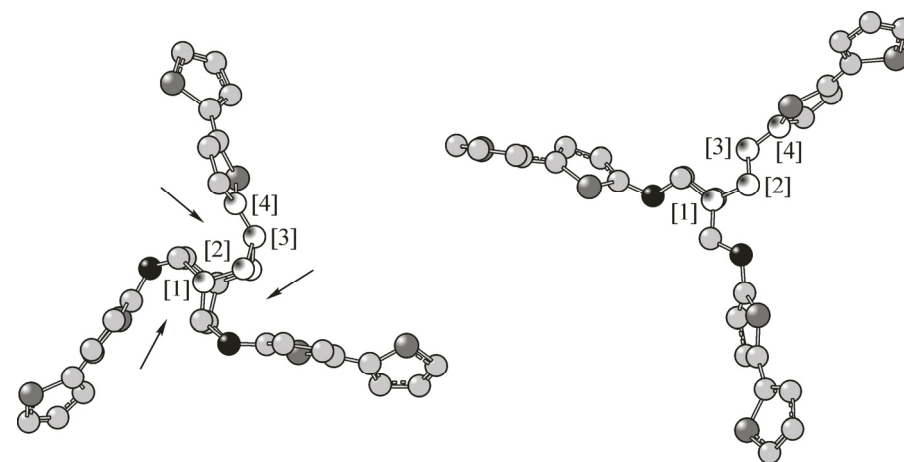*Fig. 5.* Clockwise and counter-clockwise motions of the rotary molecular machine

Fig. 6. Dihedral angle between the axis and the wings and the repulsive force created in the molecule (showed with arrows)

As it can be observed, the existing nitrogen inversion in aziridine attached to the axis caused the thiophene wings to rotate once clockwise and then again with the nitrogen inversion to rotate counter-clockwise. Thus, a bidirectional rotary machine with its rotation being related to nitrogen inversion

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Molecular Energies (*E*), *Energy differences* (Δ*E*), *and the dihedral angles between the* (C—C—C—C) *axis and the wing units of the rotary molecular machine*

Structure	*E*, Hartree	*E*, kcal/mol	Δ*E*, kcal/mol	C—C—C—C, deg.
a	−3773.7220926	−2368010.61	28.53	39.52
b	−3773.7675607	−2368039.14	0.00	150.09

was created. The evaluation of energy data obtained from the *ab initio* calculation using the Hartree—Fock method and the 6-311G** basis set showed that (b) conformation was about 28.53 kcal/mol more stable than (a) conformation. As can be seen in Fig. 6, in the (a) conformation, due to the wing units approaching the axis, a repulsive force was generated in several parts of the molecule, resulting in less stability of the (a) conformation as compared with the (b) conformation. The structural information obtained from the *ab initio* calculation using the Hartree—Fock method and the 6-311G** basis set and a comparison of the dihedral (C—C—C—C) angles between the axis and the wing units in the optimized conformations of the molecular rotator showed that the bite angle in the (a) conformation in Fig. 6 changed from 39.52 to 150.09° in the (b) conformation (Table 1). These results made it clear that the use of nitrogen inversion could produce angle changes that caused the clockwise and counterclockwise rotary motions in the designed molecular rotator.

CONCLUSIONS

As it can be noticed in the calculations, nitrogen inversion can be used as the initial motion to produce more diverse moves in a series of joined molecules. The connection of thiophene units to aziridine as the wing units and then to the hydrocarbonic axis form a molecular rotary which performs bidirectional rotating moves once energy was applied to overcome the nitrogen inversion barrier. The results obtained from this study showed that the use of nitrogen inversion could produce an angle changing domain that caused the clockwise and counterclockwise rotary motions in the designed molecular rotator.

Since the inversion barrier in aziridine is related to its substitution with the consequence of having different speeds of inversion performances, the speed can be controlled by making use of either aziridine with appropriate substitutions or any nitrogen compound replacing aziridine as the initial starter of the moves in the molecular rotary.

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