

# Electrical Rectification

## A Tale of Two Isomers

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Owing to the saturation of the efficiency of silicon devices in electronics industry, molecular electronics has gained tremendous impetus in recent times. Theoretical predictions and experimental realizations of such systems have given birth to a new generation of miniaturized electronic devices. Organic molecules with delocalized  $\pi$ -electrons show a promising future in this aspect. The long-standing history and interesting properties of two isomeric organic molecules, naphthalene and azulene, motivate us to explore their electrical conductance property and possible electronic device applications that exploit the unique characteristics associated with their structural aspects. Single molecule of azulene shows higher conductivity than naphthalene. The charge transfer from the seven-membered ring to the five-membered ring in azulene gives the system aromatic stability, making it dipolar. As a consequence, the conductance becomes asymmetric for forward and reverse bias, opening an efficient application of azulene as molecular rectifier in electronic device fabrication.

### Introduction

Research in the field of nanoscience has been of great interest in recent times, largely owing to the fact that silicon electronics is fast approaching a roadblock, because of fundamental limits set by the laws of physics and chemistry as well as the cost of production [1]. Till now, the semiconductor microelectronics fabrication has been achieved through the 'top down' lithographic



approach which involves the miniaturization of existing silicon-based chips. However, this rate of downscaling leads to reduced device performance because the issues related to quantum tunneling, interconnect delays, gate oxide reliability, and excessive power dissipation start playing a major role at such small length scales. Although some of these issues can be overcome by improving the device design, the increasing cost of fabrication has motivated research in other directions. It has led to the replacement of the ‘top-down’ lithographic approach by a ‘bottom-up’ synthetic chemical approach of assembling nanodevices and circuits directly from their molecular constituents, leading to the next generation of electronics known as molecular electronics [2–4]. In fact, recent advances in experimental techniques have allowed fabrication and measurement of current through single molecules with precision and consistency. Various molecules have already been demonstrated to behave as wires, switches, diodes, RAMs, etc. In most of the experiments, the nanoscale material is an organic molecule or a  $\pi$ -conjugated polymer. Many theories too have been developed from empirical to semiempirical and *ab initio* level to describe the electronic response functions of the nanoscale systems [5–11].

The ability of a molecule to switch between off and on states is one of the most important applications of these nanoscale materials. Experimentally, this has been observed in many organic molecules with various donor and acceptor substituents. Such unusual and interesting behaviour of organic molecules with donor and acceptor moieties stimulates the study of electronic conduction in azulene molecule along with its isomer, naphthalene [12].

### Aromatic Stability

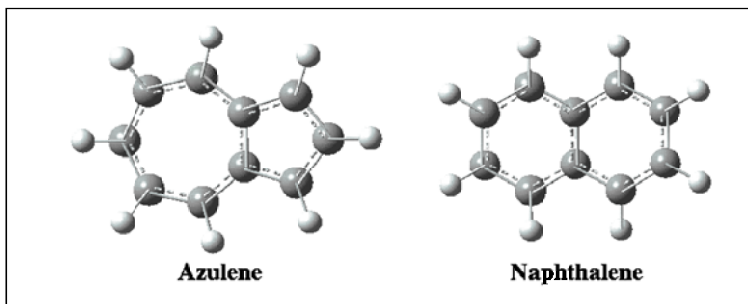
Naphthalene and azulene are two isomers with chemical formula  $C_{10}H_8$  and possessing the same number (ten) of

### Keywords

Molecular electronics, azulene, donor-acceptor structure.



**Figure 1.** Structure of two isomers, azulene and naphthalene.

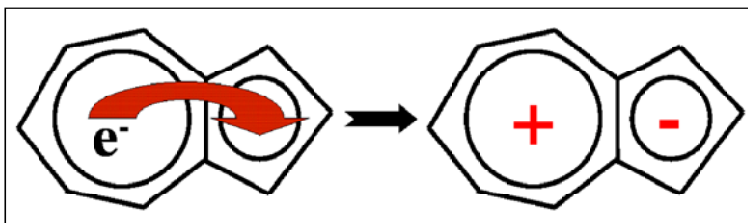


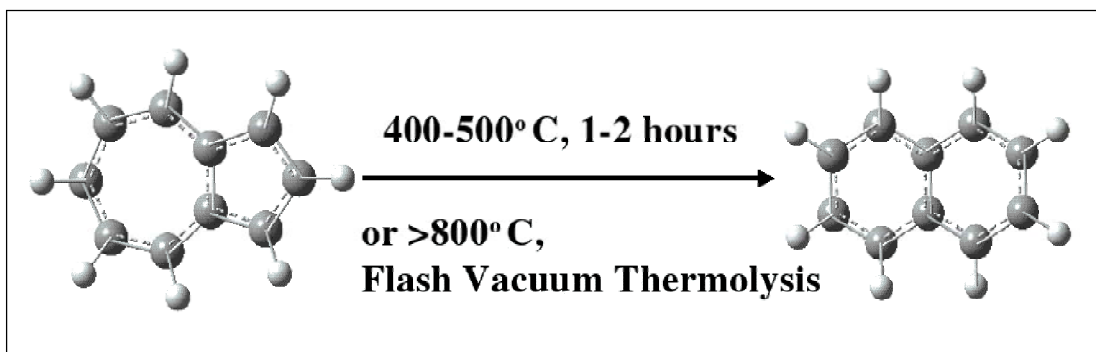
$\pi$  electrons. The geometry of the azulene molecule consists of fused five- and seven-membered rings, whereas naphthalene is made of two fused benzene rings as shown in *Figure 1*. Each six-membered planar ring in naphthalene has six  $\pi$  electrons, satisfying the criterion of Huckel aromaticity which requires  $(4n + 2)$   $\pi$  electrons in each ring. Whereas, in the case of azulene neither of the fused rings satisfies the  $(4n + 2)$   $\pi$  electrons rule. So, to gain aromatic stability, one electron moves from the seven-membered ring to the five-membered ring, resulting in six  $\pi$  electrons in each of the fused rings. As a consequence, the azulene becomes a dipolar composite system of tropylium cation and cyclopentadienyl anion, as shown in *Figure 2*.

### Thermal Rearrangement

Both these compounds, with a history of over a hundred years, have been of great interest in many ways. One of the important phenomena in this context is the thermal rearrangement of azulene to naphthalene, reported for the first time in 1947. It is a beautiful example of conversion of one nonbenzenoid aromatic compound to its benzenoid isomer. Static thermolysis above 400°C or

**Figure 2.** To gain aromatic stability, one electron moves from the seven-membered ring to the five-membered ring, making the azulene system dipolar.





flash vacuum thermolysis above 800°C transforms azulene into naphthalene (see *Figure 3*). Numerous  $^{13}\text{C}$ -labeling studies on azulene and substituted azulenes suggest different mechanisms including unimolecular and radical pathways for this rearrangement. However, none of them can explain all the experimental observations without ambiguity, suggesting a complex potential energy surface for this reaction. The most acceptable route is known as norcaradiene mechanism, proposed by Becker *et al.* It first yields a norcaradiene, then a vinylidene intermediate and finally a stable phenylbutenyne intermediate. All the three structures can rearrange to end up as naphthalene. The theoretical reaction coordinates with detail energy characteristics can be found in [13].

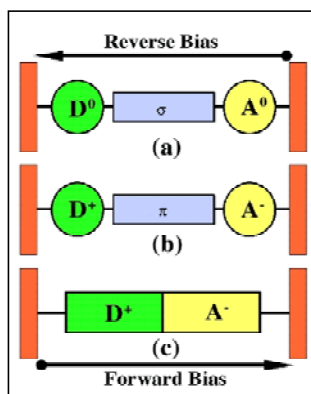
**Figure 3.** The thermal rearrangement of azulene to naphthalene.

### Charge Transfer Induced Donor-Acceptor Property

Due to aromatic stabilization via charge transfer, azulene appears intense blue. On the contrary, due to symmetric charge distribution, naphthalene appears colorless. Azulene exhibits many interesting features like fluorescence, large hyperpolarizability, etc., because of its large ground state dipole moment ( $\mu = 0.8 - 1.08D$ ) [14]. The process of gaining aromatic stability induces inherent donor and acceptor properties on the two rings of azulene, making the system a potential electrical rectifier.



**Figure 4. The schematic representation of the rectifier systems considered:**  
 (a)  $D^0 - \sigma - A^0$  [15],  
 (b)  $D^+ - \pi - A^-$  [16] and  
 (c)  $D^+ - A^-$  (present case).  
 The direction of the applied electric fields are represented by arrows, heading towards the positive bias according to the convention adopted here.



In 1974, Aviram and Ratner [15] first suggested that a single molecule with a donor( $D$ )- $\sigma$  spacer-acceptor( $A$ ) structure would behave as a  $p$ - $n$  junction diode when placed between two metal electrodes. After almost two decades, Metzger *et al* [16] studied Langmuir–Blodgett (LB) films of  $\gamma$ -( $n$ -hexadecyl) quinolinium tricyanoquinodimethanide ( $D$ - $\pi$  spacer- $A$  species) between metal electrodes and demonstrated the proposed rectifying behavior. However, the systems considered in those two cases are fundamentally different. In the former case, the neutral donor and acceptor are separated by one  $\sigma$ -spacer, whereas in the experimental case [16], the molecule is in a zwitterionic form where the positive and negative charges are located on the donor and the acceptor respectively, separated by one  $\pi$ -spacer. The schematic representation of these two systems are shown in Figures 4(a) and (b) respectively. In both the cases, the reverse bias current has been found to be more compared to the forward bias, suggesting potential rectifying behavior. In the present study, the azulene system resembles the system considered by Metzger *et al*, with charge separation on donor and acceptor, but lacking any spacer in between as shown in Figure 4(c). The possible electron transfer mechanism in Metzger's system is discussed in the following steps,

- (i)  $L | D^+ - \pi - A^- | R, \longrightarrow L | D^0 - \pi - A^0 | R,$
- (ii)  $L | D^0 - \pi - A^0 | R \longrightarrow L^- | D^+ - \pi - A^- | R^+,$

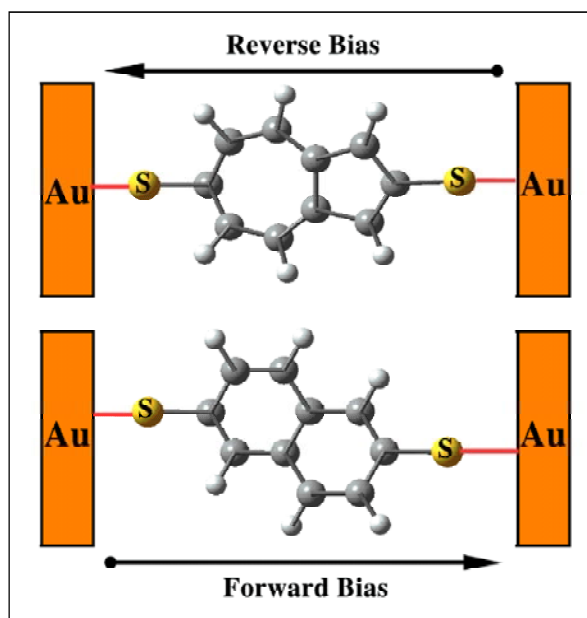
where  $L$  and  $R$  are left and right electrodes respectively. The above steps suggest an intervalence transfer of one electron from the negatively charged acceptor moiety to the positively charged donor moiety, followed by the electron transfer from right electrode to the acceptor and donor to the left electrode in concerted way. The flow of electrons in opposite direction under the influence of forward bias requires the transfer of electrons from left electrode to donor and acceptor to right electrode

followed by the intervalence transfer of one electron from the donor moiety to the acceptor moiety. However, these steps for electron flow under forward bias are found to be less likely compared to that for the reverse bias [15,16].

### Electrical Rectification: Azulene and Naphthalene

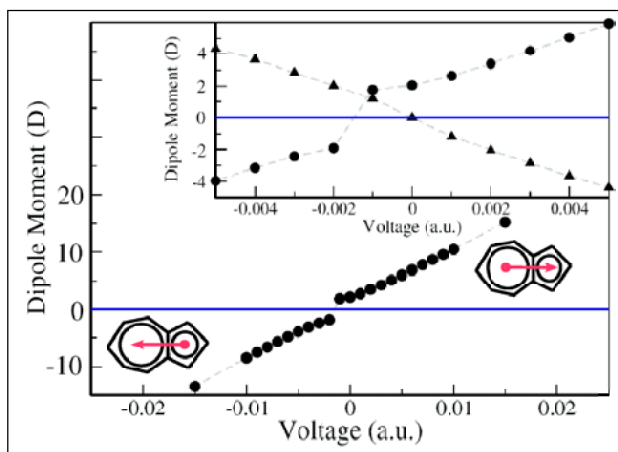
Advances in synthesis of designer organic molecules, device fabrication techniques and sophisticated measurements have made possible the experimental realization of passing an electrical current through a single molecule. Charge transport through molecules can now be probed in a controlled way and several prototype devices such as conducting wires, rectifiers, switches and transistors have already been developed.

For molecular electronic device fabrication, one needs to attach the molecules between two electrodes. The most common way to anchor the organic molecules to gold electrodes is the use of thiol linkers. In the present case too, the thiol linkers are attached to the molecules at the farthest positions possible as shown in *Figure 5*.



**Figure 5.** Electronic devices using thiolated naphthalene and azulene molecules anchored between two gold electrodes. The direction of the applied electric fields are represented by arrows, heading towards the positive bias according to the convention adopted here.

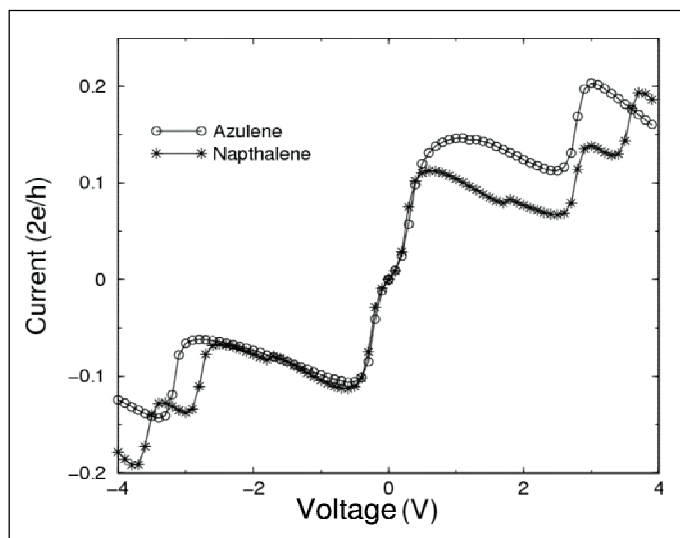
**Figure 6.** Variation of dipole moment (in Debye) of the azulene system as a function of electric field (in a.u., where 1 a.u. = 51.422 Volt/Å). The dipole moment directions under forward and reverse bias are shown by the arrows. Inset shows the dipole moment for both azulene (circle) and naphthalene (triangle) in a smaller bias window.



The strong bonding between gold and sulfur facilitates such device fabrication. The attachment of the anchoring thiol groups in other positions may result in different electronic structures and consequent electrical responses, as observed for other systems because of quantum interference [17]. However, in the present context, we will emphasize on the difference in conductance between azulene and naphthalene, while connected to the electrodes symmetrically. The I-V characteristics can be studied using the non-equilibrium Green's function method, already widely reported in the literature [18]. The electric field in the present case has been applied along the long axis of the molecules as shown in *Figure 5*, as a ramp potential<sup>1</sup>.

<sup>1</sup> Potential with linearly varying gradient.

The ground state dipole moment of azulene changes differently for the electric field in either directions. From *Figure 6*, it can be seen that, in the absence of electric field, the azulene molecule has remanent dipole moment which increases with increasing electric field in the forward (+ve) bias direction. However, with increasing electric field in the reverse (-ve) bias direction, it decreases initially and then shows a steady increase in the opposite direction. These observations are in agreement with the fact that the electron flows from the seven-membered ring to the five-membered ring easily compared to the opposite direction because of its aromatic



**Figure 7.** Current as a function of voltage for azulene and naphthalene molecules with two terminal thiol groups.

stability. However, the electric field in the reverse direction forces the electrons to move from the five-membered ring to the seven-membered ring at the expense of aromatic stability and thus the dipole moment reduces from the ground state value initially for lower bias. Further increase in bias in this direction accumulates the charge on the seven-membered ring resulting in a dipole moment increase in that direction. But the dipole moment of naphthalene molecule increases with increasing bias in both directions symmetrically from the zero dipole moment ground state position at zero field, as can be seen in the inset of *Figure 6*.

Both azulene and naphthalene systems show step-like behavior in current-voltage characteristics, as can be seen from *Figure 7*. These are the eigenvalue staircases that appear whenever the electrochemical potential of the electrodes comes in resonance with the molecular levels [2]. In lower bias regime, both molecules show nearly the same current. Beyond a certain forward bias value, the azulene system shows more current than the naphthalene system. But for reverse bias, the current of azulene system becomes lower than that of naphthalene. It is due to the fact that bias along +ve direction drives





the electrons easily from the seven-membered ring to the five-membered ring, giving the system aromatic stability. Whereas reverse bias drives the electrons opposite to the dipole moment direction. So, the mechanism for the electron flow under the influence of forward bias, as described earlier becomes more likely in case of azulene. Because of this asymmetric current-voltage characteristics, azulene promises to be a good candidate for possible use in electrical rectification. On the other hand, due to symmetric electron cloud distribution over the two six-membered rings, naphthalene shows symmetric current-voltage behavior in both the bias directions. At higher bias values the current shows a considerable decrease with increase in bias, since the external bias localizes the electrons, reducing the charge flow.

### Summary

The interesting charge transfer phenomenon makes azulene distinct in many aspects compared to its isomer naphthalene. It is observed that the azulene molecule with its intrinsic donor-acceptor structure, shows efficient electrical rectification. Molecules such as azulene are thus promising candidates to develop novel molecular electronic devices <sup>2</sup>.

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<sup>2</sup> The quantitative estimation of dipole moments has been obtained from *ab initio* quantum chemical calculations using the density functional methods in the program package *Gaussian-03* [19]. The calculations for current-voltage characteristics have been performed using non-equilibrium Green's function [18]. All the calculation details are given in [5,12]



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