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## Can Aromaticity Enhance the Electron Transport in Molecular Wires?

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### Abstract

An interesting debate has been recently raised around the role played by aromaticity in the electron transport ability of molecular wires. Normally, it is associated to destructive interference effects, so that the more aromatic the wire the less conductor. This rule was observed experimentally in a series of homologous wires containing ring units of different aromaticity, but theoretical calculations and other recent experiments demonstrate the rule cannot be generalized and depends, for instance, in the type of molecule-electrode contact. However, neither chemical explanation nor qualitative rules were given yet to allow predicting the specific behaviour of different molecular junctions. In this work, using series of polymeric molecular wires of different length and formed by different aromatic units, it is proven how it is possible to change from an expected destructive to a constructive interference effect of the aromaticity in the electron transport. Thus, aromaticity may be also employed to enhance the electron transport in a molecular wire. A chemical explanation to the experimental and theoretical observations is given and a simple way of tuning the response of a molecular wire to an external electric voltage by increasing/decreasing its aromaticity and changing its type of molecule-electrode contact is provided.

**Keyword:** electron transport, aromaticity, molecular wires, polymeric wire

## 1. Introduction

Quantum methods have emerged as essential tools for the development of molecular electronics [1–15]. They allow interpreting and predicting the behavior of different organic structures linked to metallic electrodes (molecular junctions) and subjected to an external bias voltage. The development of methodologies based on the quantum theory to calculate the molecular electric conductance and/or related properties, goes in parallel with the recent technological achievements that have made possible to measure the electric conductance, experimentally, in molecular junctions formed by a large number of different organic system [16–24]. Theoretical methods bring up the possibility of understanding the conductance in terms of the chemical properties of the molecules involved. The electron transport ability of a molecular junction can be rationalized by using extended properties such as electron conjugation, aromaticity or polarizability, which can be understood in terms of the electronic structure and geometric arrangement [25–34]. The establishment of a straightforward relation between our chemical understanding and the molecular electric conductance is therefore one of the main targets in the design of electronic devices constructed from individual molecules. Using this 'a priori' knowledge, quantum methods may contribute more efficiently to the development of molecular electronics.

Recently, Venkataraman et al analyzed experimentally the effect on the electric conductance of an essential property of some conjugated organic systems, namely, the aromaticity [28]. Using a series of model molecular junctions, they found a destructive effect of the ring aromaticity over the electric conductance, reflected in a negative relationship between conductance and aromaticity. This relation was stated by evaluating molecular junctions involving different five-member rings, cyclopentadiene, furan and thiophene and theoretically justified in a previous work by Xie et al [31]. In addition, in a further work, this destructive relation was also observed in other junctions [32], and the observation was turned into a rule, the NRCA rule (negative relationship between conductance and aromaticity). However, a recent theoretical study showed that this correlation between aromaticity and conductance is not always fulfilled, finding different trends when other anchoring groups are employed to connect the molecule to the electrode [30]. These theoretical results were obtained with the non-equilibrium Green's functions (NEGF) method in combination with density functional theory (DFT). The study concluded with the rejection of a general rule for the relation between aromaticity and conductance, however, the different behaviors observed were just highlighted but not explained. It must be noticed that theoretical results in contradiction with the NRCA had been also published even before the experimental observations that gave rise to this rule [27, 29]. In these previous works, it had been found that the kind of molecule-metal contact may confer a completely different behavior to the electron transport ability of polyphenyl chains of increasing size. Thus, increasing the number of phenyl units the electric conductance may be enhanced or diminished depending on the nature of the anchoring

element. However, the effect on the conductance of changing the phenyl units by other rings of different aromaticity has not been investigated yet. Merging these two structural modifications, namely, the number of aromatic units and its degree of aromaticity, may provide a definite picture of the rule played by this fundamental property in the electron transport ability of organic molecular chains.

Herein, in this work the relation between aromaticity and electric conductance is evaluated in the junctions proposed by Venkataraman et al [28] and in molecular chains of increasing size formed by five-member rings of different aromaticity; pyrrol, furan and thiophene. The same types of binding with the metal contact (gold in this work) employed in the previous works using polyphenyl chains were considered here[29]. In one of them, the contact is done directly between a carbon atom from the ring and a gold atom, whereas in the second one a methylene unit is employed as anchoring group. In the following section, the methodologies employed to determine the electric conductance and the ring aromaticity are described, then, the results are presented and discussed in the next section and, finally, the main conclusions are summarized in the last point.

## 2. Methodology

All the structure optimizations and wavefunction calculations were performed in the framework of the density functional theory (DFT) with the B3PW91/LANLD2Z level, using the Gaussian 09 program [35]. A bias voltage ranging from 0V to 2V was simulated by applying a constant electric of appropriate intensity along the imaginary line that connects the two metal contacts. The electron transport ability was analysed using the Landauer formalism [36], with the transmission channels constructed by electron deformation orbitals (EDOs) [37, 38]. This method [38] is a generalization of the calculation of the quantum conductance from the time-energy uncertainty relation [39] and has been implemented in a code written in FORTRAN.

Multicenter delocalization indices, n-DI, were employed as indicators of aromaticity of the studied rings [40–42]. They represent a measure of the electron delocalization or electron sharing in a set of atoms, which, when conforming a ring structure, provides a measure of the cyclic electron delocalization intrinsically related to the aromatic character [43]. In order to calculate n-DIs, the molecular space was partitioned in atomic domains using the Hilbert space. Hence, the electron population is distributed among the atoms based on the location of the corresponding basis functions, in a similar way as the Mulliken partitioning scheme of the electron density [44]. This fact makes the method strongly dependent on the basis set employed, and it is not recommended with basis sets including diffuse functions. However, it is appropriate for this work, where the aromaticity is studied in relative terms within the different systems investigated and the basis set employed does not include diffuse functions. Using the Hilbert space the n-DI is obtained by the following expression;

$$\text{n-DI} = 2n \sum_P \sum_{i \in A} \sum_{j \in B} \sum_{k \in C} \dots \sum_{m \in M} (\mathbf{PS})_{ij} (\mathbf{PS})_{jk} \dots (\mathbf{PS})_{mi} \quad (1)$$

where  $\mathbf{P}$  is the density matrix and  $\mathbf{S}$  the overlap matrix, the product of both,  $\mathbf{PS}$ , is sometimes known as the charge-bond order matrix. The first summation in Eq 1. runs over all the non-equivalent permutations of the n atoms. The remaining summations run over the basis functions,  $i, j$ , etc, centered on the atoms A, B, etc. Currently, the n-DIs are considered a very trustable measure of the electron delocalization along a string of atoms, which is the essence of the aromaticity concept when applied to cyclic structures. As an example, they have been implemented and successfully applied by different theoretical groups to investigate the aromaticity of typical organic molecules [40–43, 45–50], metallic clusters[51, 52], transition states in pericyclic reactions[53, 54], porphyrins[55, 56] and homoaromatic systems [57].

### 3. Results

#### 3.1. Relation of Aromaticity and Conductance

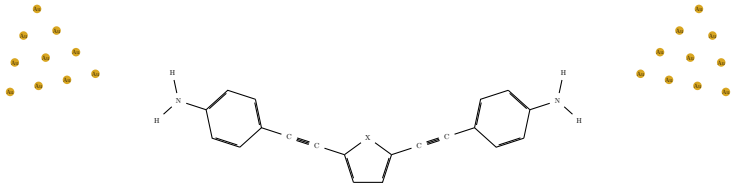
Previously, Venkataraman et al [28] measured the molecular electric conductance in three single-molecule junctions, each containing a different 5-member ring (thiophene, furan and 5,5-dimethylcyclopenta-1,3-diene). Within their proposed systems, the effect of the aromaticity of the 5-member ring in the conductance was quantified, finding an inverse relation between them.

In the structures proposed by Venkataraman et al, the order of aromaticity for the different 5-member rings was considered to be the same as that of the isolated rings, ignoring the effects of the chemical environment. Therefore, the thiophene ring was supposed to be the most aromatic, followed by the furan and the 5,5-dimethylcyclopenta-1,3-diene rings, respectively. This order has been checked in this work by means of the 5-DI values calculated for the isolated rings and for the structures proposed in ref [28], finding the same relation of aromaticity in both cases. This confirms not only that the order of aromaticity proposed based on the aromaticity of the isolated rings was correct, but also that the choice of our method in order to measure this property is adequate.

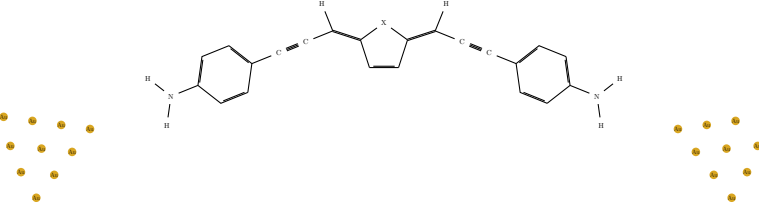
Calculation of the electric conductance in these structures non-covalently attached to metal clusters formed by ten gold atoms are given in Table 1. In the calculations, we have employed the same voltage as in the experiments (0.225V) and a larger voltage (2V) in order to enhance the differences found between the different aromatic rings. The results agree with the experimental findings using both voltages, and the conductance decreases as the aromaticity of the central ring increases. However, this negative conductance/aromaticity relationship is not general and a positive relationship is found when a methylene unit is inserted between the aromatic ring and the acetylene group (see Table 1).

To analyze the reason of this opposite behavior, we have considered in this work a set of simpler structures where only the aromatic fragments responsible of the change in conductance and the metal-molecule contacts are preserved. Thus, the electronic conductance has been measured for structures involving different heterocyclic aromatic units such as Pyrrole, Furan and Thiophene attached to gold atoms. On one hand, the pP like contact is established between a carbon atom of the ring and a gold atom of the electrode. On the other hand, the pX<sub>2</sub> like contact involves a methylene carbon atom, which bridges covalently the ring with two atoms of the electrode. For these systems, the influence of the aromaticity in the conductance was evaluated. In the case of carbon linkers, the molecule-metal contact is a covalent bond [58, 59].

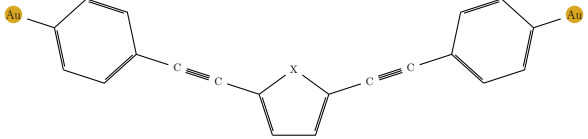
Table 1: Electric Conductance at 0.225V and 2V, 5-DIs of the central aromatic ring, and energy gap between the occupied and virtual MOs involved in the electron transport for the structures analyzed in reference [28] and those formed by replacing the amino group linkers by covalent carbon-metal contacts



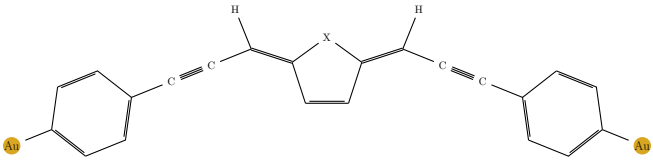
X	G ( $\mu S$ ) 0.225V	G ( $\mu S$ ) 2V	5-DI	$\Delta E$ (eV)
S	0.484	21.245	6.075E-01	0.170
O	0.499	22.401	5.899E-01	0.171
C(CH <sub>3</sub> ) <sub>2</sub>	0.504	22.959	7.568E-02	0.152

X	G ( $\mu S$ ) 0.225V	G ( $\mu S$ ) 2V	5-DI	$\Delta E$ (eV)
O	0.586	29.387	2.877E-01	0.145
S	0.530	28.902	2.251E-01	0.148
C(CH <sub>3</sub> ) <sub>2</sub>	0.499	24.526	5.472E-02	0.163

X	G ( $\mu S$ ) 0.225V	G ( $\mu S$ ) 2V	5-DI	$\Delta E$ (eV)
O	0.665E-02	0.524	6.377E-01	3.29
S	0.718E-02	0.566	5.868E-01	3.15
C(CH <sub>3</sub> ) <sub>2</sub>	0.791E-02	0.625	3.454E-02	2.80

X	G ( $\mu S$ ) 0.225V	G ( $\mu S$ ) 2V	5-DI	$\Delta E$ (eV)
O	0.888E-02	0.854	2.386E-01	2.44
S	0.924E-02	0.625	1.723E-01	2.46
C(CH <sub>3</sub> ) <sub>2</sub>	0.720E-02	0.569	6.093E-02	2.85

In order to check the influence of the covalent or non-covalent nature of the contact, we have first analyzed the conductance/aromaticity relationship in the experimental structures previously reported by Venkataraman et al. but replacing the amino linkers by a covalent carbon-gold contact. The results are collected in Table 1, as one can see the same negative relationship is found for the original structures, whereas a positive relationship is found for

the structures including a methylene unit between the aromatic ring and the acetylene group. Very revealing is to find out that this reversal in the conductance order is also reflected in a reversal in the energy gaps of the occupied and virtual molecular orbitals involved in the main transmission channel[38]. Thus, in the original structures investigated experimentally the energy gap follows the order cyclopentadiene < furan  $\approx$  thiophene, but introducing the methylene group the order is furan < thiophene < cyclopentadiene. This opposite behavior is even more clear in the structures formed by replacing the amino linkers by covalent carbon-gold contacts, but in this case the energy gaps are significantly larger, which explains also the smaller conductances.

The simplified structures further studied in this work were built alternating ring units as shown in the schemes of Figure 1. Their geometry optimizations were performed upon constraining to its highest symmetry point group;  $C_{2v}$  for those structures with odd number of rings and  $C_{2h}$  for those with even number of rings. Despite this restriction, all the thiophene and furan structures were found to be minima with both linkers. However, in the pyrrole chains, the structures were not minima when the number of rings was  $n \geq 2$  with the pP linker and  $n \geq 3$  with the pX<sub>2</sub> linker. When these structures were optimized without any symmetry constrain a small distortion in the coplanarity of the rings was found. This effect is caused by the interference of hydrogen atoms of the ring and the amine hydrogen. A similar distortion was found for the structures investigated in Ref [28], being the cause of the anomalous conductance results obtained according to the expected behavior. In order to avoid this structural impact and evaluate only the electronic effects in the conductance of the system, the structures employed for the calculations were those obtained under symmetry restrictions.

The 5-DIs obtained for the ring structures investigated in this work are collected in Figure 1. The results show that the most aromatic ring is pyrrole, followed by furan and thiophene using both the pP and pX<sub>2</sub> linkers. Thus, the chemical environment of the ring in the molecular junction is responsible of the change in the aromaticity order with respect to the isolated rings. In order to check the role played by aromaticity in the electron transport ability of these systems, the electric conductance was calculated by subjecting them to an external bias voltage ranged between 0V to 2V.

The results obtained for the shortest chains ( $n=1$ ) with the pP linker are collected in Figure 2-(a). The  $G/V$  profiles reflect the expected behavior according to Ref. [28, 32], being the thiophene structure, which is the least aromatic, the one with largest conductance, followed by the pyrrole and furan structures whose  $G/V$  profiles are mostly overlapped. Using the pX<sub>2</sub> linker, an opposite behavior is shown. Therefore, a positive relationship is found between the aromaticity of the ring and the conductance, being the pyrrole structure the one with largest conductance and aromaticity, followed by furan and thiophene structures, respectively, as shown in Figure 2-(b).



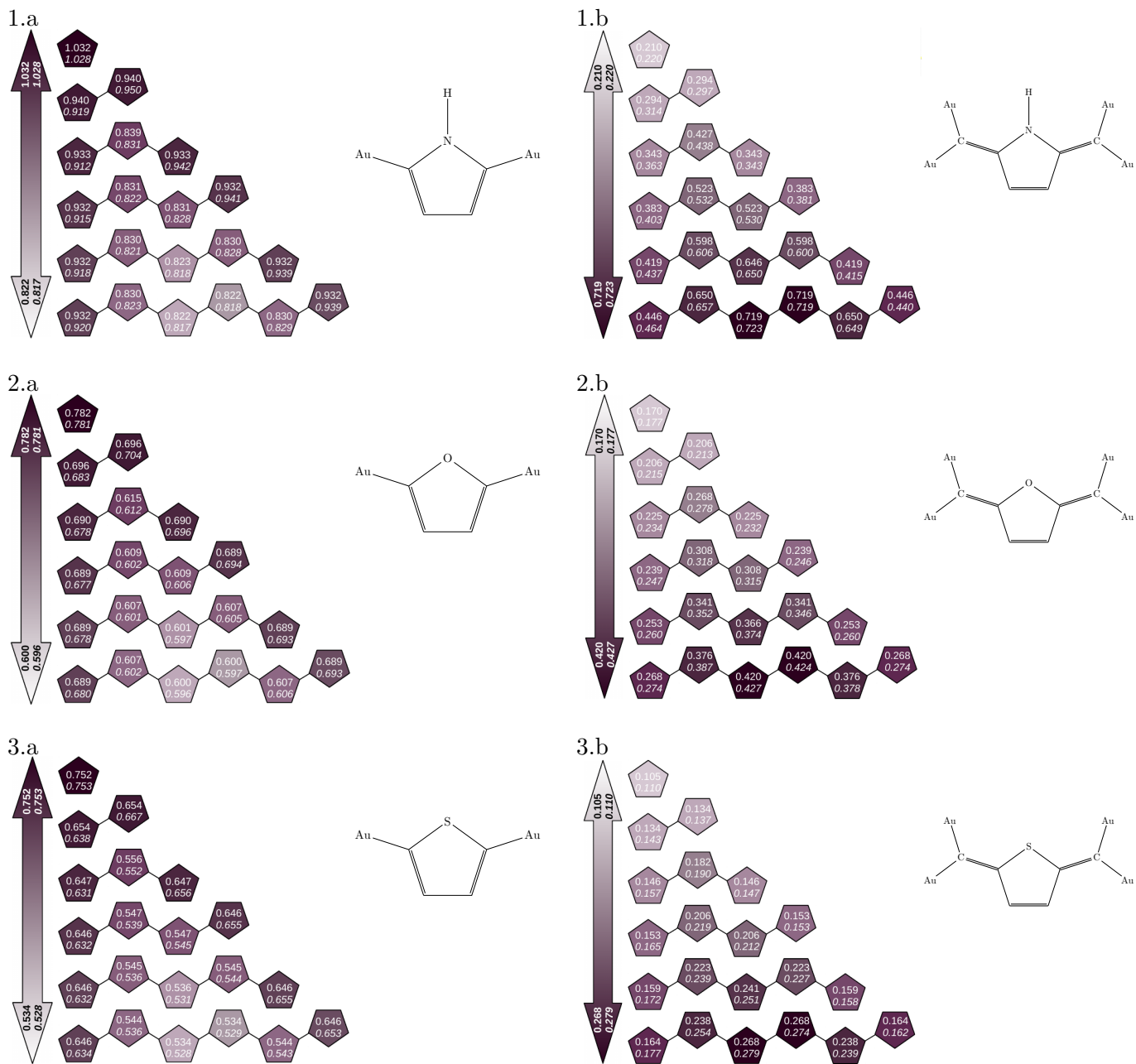


Figure 1: 5-DIs of the aromatic rings in the structures with  $n=1-6$  units for (a) pP and (b) pX<sub>2</sub> like linkers.

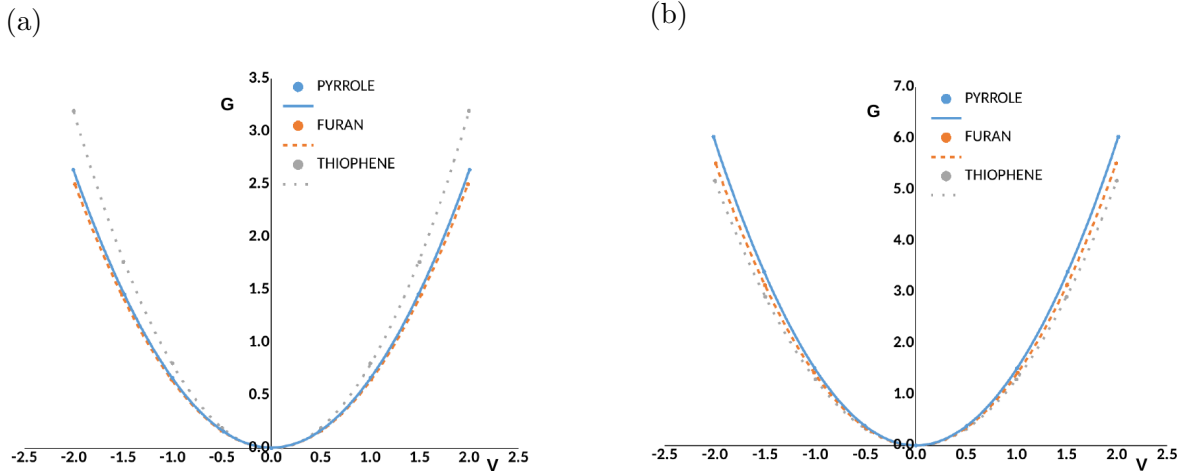


Figure 2:  $G$ (in  $\mu\text{S}$ ) vs  $V$ (in Volts) profiles obtained for the Pyrrole, Furan and Thiophene structures with the (a) pP and (b) pX<sub>2</sub> linker.

In addition, it must be also noticed that the conductance is significantly larger with the pX<sub>2</sub> linker than the pP one. This observation can be understood in the framework of a qualitative Valence-Bond (VB) model, which considers only neutral and polarized alternant conjugated structures. The polarized structures shown in Figure 3 are responsible of the conductance of the system under an external field. It can be observed that in those systems with a pX<sub>2</sub> linker, the polarized structures tend to increase the ring aromaticity of the systems, and vice versa for those systems with a pP linker. Therefore, the conductance in pX<sub>2</sub> is favoured by an increase in the aromaticity whereas in pP occurs the contrary. This qualitative model is supported by the changes experienced by the 5-DIs upon the application of the external electric voltage (Figure 1). Thus, the external voltage induces a general reduction of 5-DIs in pP chains, with the exception of some rings attached to the positive gold electrode. On the contrary, the voltage induces a general increase of 5-DIs in pX<sub>2</sub> chains, again with the exception of some rings attached to the positive gold electrode.

Thus, the opposite conductance/aromaticity relationship observed for the two linkers can be also understood in terms of aromatic stabilization. For wires with the pX<sub>2</sub> linker, the polarized structures responsible of the conductance contribute to aromaticity, stabilizing the system. The larger the stabilization of the polarized structures, the larger its weight in the VB wavefunction, and therefore the better its conductance. However, in the structures with the pP linker, the opposite behavior is found. In these systems, the formation of the polarized forms will be associated to a loss of stability produced by a decrease of aromaticity. The weight of the polarized structures will be larger for those rings with a lower loss of aromaticity and therefore a lower destabilization. This is the case of the least aromatic ring, thiophene,

which shows the largest conductance.

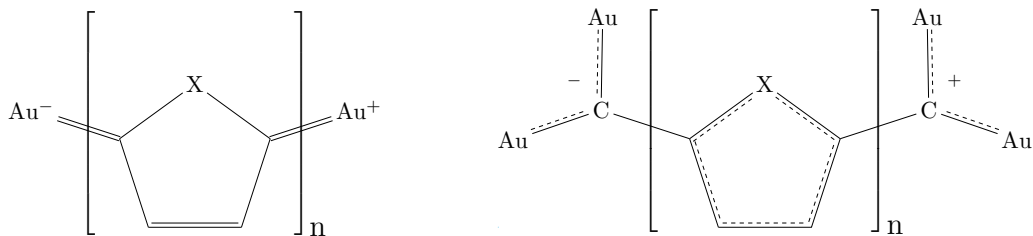


Figure 3: Polarized conjugated structures of the molecular junctions with pP and pX<sub>2</sub> like linker.

Thus, we can state that the relationship between the aromaticity of a system and its conductance is not such a straightforward and, which is more important, is not general, depending on the nature of the linker. Alternatively, the electric transport ability of conjugated molecular wires can be estimated qualitatively using the simplified VB model proposed above, which requires only a quick look at the nature and weight of the polarized structures. Those systems in which polarized structures at the contacts increase the aromatic stabilization will show a larger ability to transport electrons and a positive conductance/aromaticity relationship.

### 3.2. Length Chain Effects

The effect of the chain's length in the relationship of aromaticity and conductance was carefully evaluated. In the structures with the pX<sub>2</sub> linker, the 5-DIs increase significantly with the number of units, being the inner rings those with larger delocalization (see Figure 1). On the contrary, in the structures with the pP linker, the opposite trend is observed, being the 5-DIs slightly reduced with the number of units. For this linker, the outer rings are those with larger delocalization. These differences can be explained again by approximating the VB wavefunction as a combination of polarized and neutral conjugated structures. As the number of rings increases for pX<sub>2</sub>, the number and weight of the polarized forms increase due to the aromatic stabilization provided by them. The net effect is a significant increase of the local ring aromaticities. In the case of pP, the relative weight of polarized and neutral forms seems to keep almost unaltered along the series, with a small bent towards polarized forms reflected on a small decrease of the local ring aromaticities.

It is known that for electronic transport in mesoscopic systems, where the process is governed by scattering, the conductance of a wire decreases with its length. However, at molecular level, significant changes in the electronic structure can arise from the increase of the chain length, affecting this behavior. In order to understand the influence of the chain length, the conductance was calculated at different voltages and collected in Figure 4. Again, an opposite trend can be observed for the results obtained with different linkers. For the pP linker, the expected behavior is found as the conductance decreases with the number of ring units. Therefore, the main influencing factor, the chain length, rules the conductance of the system. Although the increase of the ring units in the pP structures causes a partial loss of aromaticity in the rings, and thus, an expected increase of conductance, this effect is clearly not enough to compensate the prevailing length chain effect.

On the contrary, the opposite trend is observed in the pX<sub>2</sub> systems, being the conductance reinforced with the number of units. In this case, the electronic effects prevail over the length chain effects. The large increase of aromaticity of the rings in the longer chains favors noticeably the conductance of the system.

Then, it can be asserted that the effects governing the electronic transport in a molecular wire are particular for each linker. For instance, in the case of pP, the essential and almost single factor accounting for the relation of conductance and the number of units in the wire is the length effect. In macroscopic conductors, the conductance can be expressed as shown in Eq. 2, where  $l$  is the length of the conductor,  $A$  is the cross-sectional area of the conductor and  $\sigma$  is the electrical conductivity.

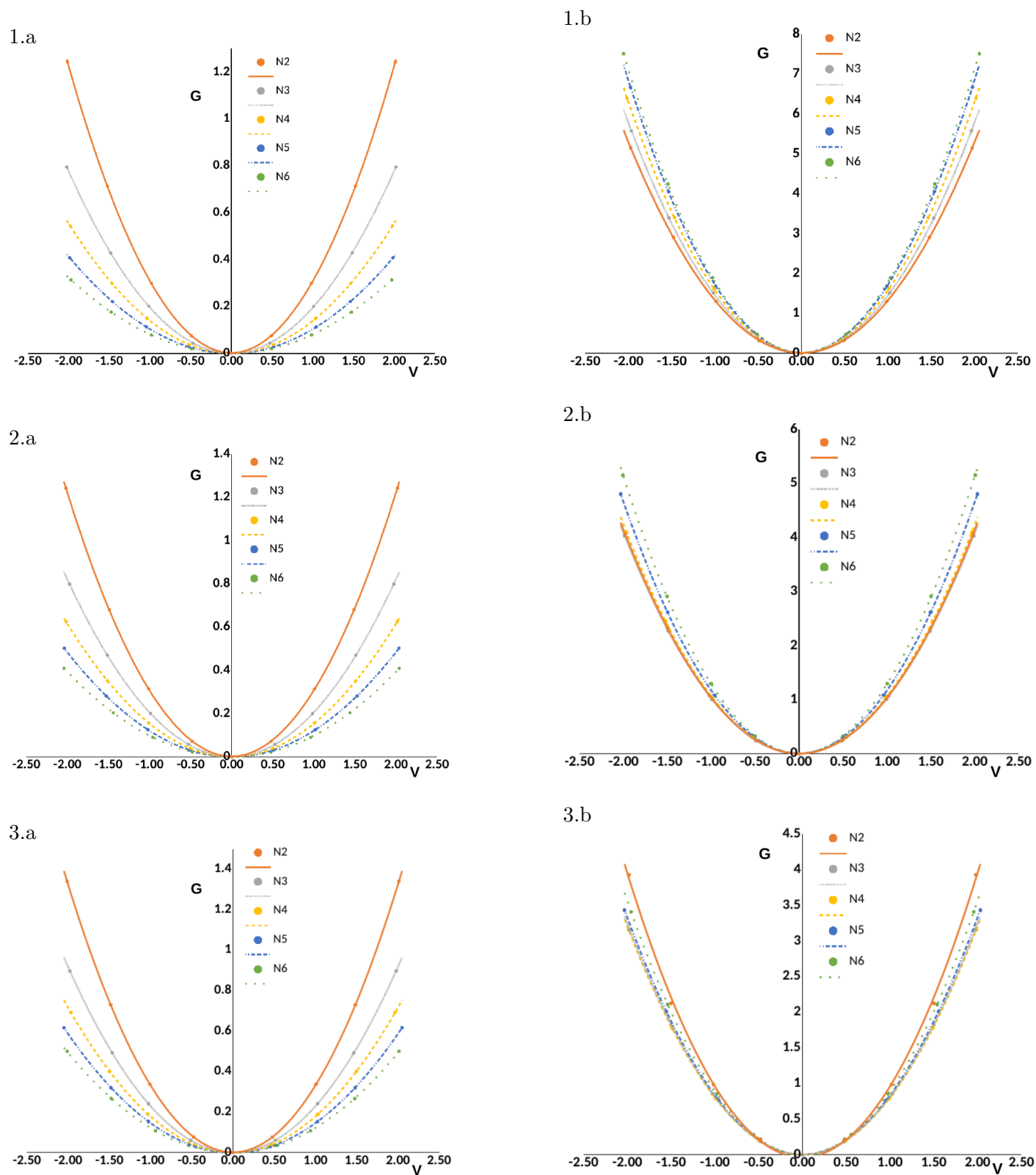


Figure 4:  $G$ (in  $\mu S$ ) vs  $V$ (in Volts) profiles obtained for the (1) Pyrrole, (2) Furan and (3) Thiophene structures with  $n=2-6$  aromatic rings and the (a) pP and (b) pX<sub>2</sub> linker.

$$G = \sigma \frac{A}{l} \quad (2)$$

For a selected voltage of 2V, the conductance of the pP structures was represented against the inverse of the number of units ( $n=1-6$ ),  $n$  taken as a measure of the chain length. The resulting chart is shown in Figure 5-(a), in which a linear relation can be observed for the structures involving the three different aromatic rings, evidencing the inversely proportional relation between conductance and chain length predicted, in macroscopic regimes, by Eq. 2. This linear relation also points out to a negligible contribution of electronic effects, which would be reflected on changes in the conductivity.

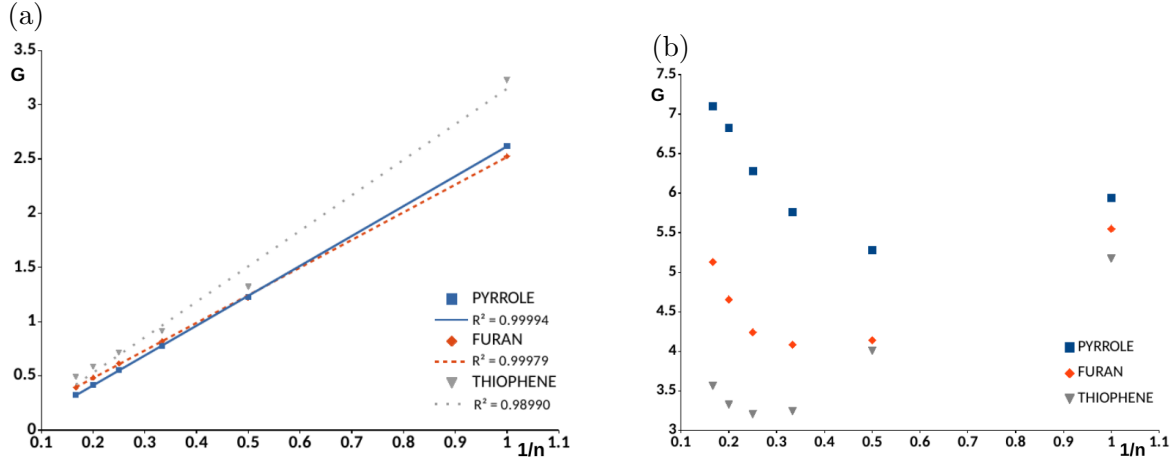


Figure 5:  $G$  (in  $\mu\text{S}$ ) obtained under a bias voltage of 2V vs  $1/n$  for chains with  $n=1-6$  units of Pyrrole, Furan and Thiophene, with the (a) pP and (b) pX<sub>2</sub> linker.

However, when the conductance is represented against  $1/n$  for the pX<sub>2</sub> structures, as shown in Figure 5-(b), a different behavior is observed. In this case, no linear relation is found. For pyrrole, it can be observed how the conductance increases with the number of units, being the structure with  $n=1$  the only outlier. This change of behavior can be explained in terms of electronic effects. For the pX<sub>2</sub> linker, the large increase of aromaticity comes with an important electronic stabilization of the system, rising its electric conductivity ( $\sigma$ ) and overcoming the length chain effect. When going from the pyrrole structure with  $n=1$  to  $n=2$ , the change in the ring aromaticity is small and then the electronic effects are not enough to govern the conductance profile. The same is found for furan and thiophene, in which the weight of the electronic effects prevail over the length chain effect as of chains with  $n=3$  and  $n=4$  units, respectively. Thiophene structures are perfect for illustrating the balance between these two opposite effects. For chains with  $n=1-3$  the aromaticity is rather

small, then the systems behave as the structures with the pP linker and a linear relation is found between its conductance and  $1/n$ . For chains with  $n > 3$ , the aromaticity of the system becomes relevant, the linear relation between conductance and  $1/n$  is no longer fulfilled and the conductance increases with the number of units.

Opposite trends between aromaticity and electron transport ability in pP and pX<sub>2</sub> chains are also found when, instead of the electric conductance, the energy gaps between occupied and virtual molecular orbitals involved in the main transmission channels are analyzed. These orbitals are the main responsible of the electron transport. The values of these energy gaps are collected, for all the pP and pX<sub>2</sub> chains, in Table 2. Thus, the energy gap follows the order pyrrole>furan>thiophene in pP chains, the smaller the aromaticity the smaller the energy gap and then the larger the conductance. On the contrary, the energy gap follows the order thiophene>furan>pyrrol in pX<sub>2</sub>, the larger the aromaticity the smaller the energy gap and then the larger the conductance. These trends are more noticeable in chains with  $n > 2$ .

Table 2: Electric conductance at 2V and energy gap between the occupied and virtual MOs involved in the electron transport of the pP and pX<sub>2</sub> chains represented in Figure 1.

		pP		pX <sub>2</sub>	
	Ring	G ( $\mu S$ )	$\Delta E$ (eV)	G ( $\mu S$ )	$\Delta E$ (eV)
n1	Pyrrole	2.621	4.52	5.943	3.20
	Furan	2.526	4.54	5.551	3.45
	Thiophene	3.228	4.36	5.173	3.43
n2	Pyrrole	1.225	4.74	5.281	2.04
	Furan	1.221	4.71	4.142	2.42
	Thiophene	1.322	4.73	4.004	2.47
n3	Pyrrole	0.777	3.81	5.762	1.35
	Furan	0.820	3.54	4.085	1.79
	Thiophene	0.916	3.18	3.244	1.91
n4	Pyrrole	0.554	3.53	6.283	0.87
	Furan	0.615	3.19	4.241	1.35
	Thiophene	0.716	2.80	3.205	1.53
n5	Pyrrole	0.414	3.36	6.826	0.55
	Furan	0.484	2.96	4.656	1.00
	Thiophene	0.587	2.57	3.330	1.24
n6	Pyrrole	0.324	3.24	7.096	0.35
	Furan	0.394	2.81	5.131	0.71
	Thiophene	0.493	2.41	3.564	1.01

This opposite relation between aromaticity and conductance according to the linker, pP or pX<sub>2</sub>, was also recognized in a previous work for *p*-phenylene and *p*-xylylene chains [29]. For these systems, the conductance of the pX<sub>2</sub> structure was found to be larger than that

of the pP. In the same study, it was also found that the increase of the length chain has associated an increase in the conductance in pX<sub>2</sub>, so as the reverse behavior for pP. Herein, we have proved that these reverse relations are intrinsically connected with the nature of the linker. This allows constructing molecular wires ranging quite different conducting abilities and chain length behaviors by tuning the aromaticity of the ring unit and the kind of linker.



#### 4. Conclusions

Previous experimental works had found an inverse relation between the aromaticity of a ring unit in a molecular wire and the conductance of the corresponding junctions formed with gold electrodes. In the present work, the electronic transport in three different heterocyclic aromatic chains has been evaluated, using two types of contacts with gold atoms. Different trends have been found for the models proposed according to the relation between conductance and local aromaticity of the rings. Therefore, the trend found by Venkataraman et al.[28] is only one of the possible scenarios, evidencing that the relation between aromaticity and conductance is not as unequivocal. In systems such as those involving pP like contacts, the local aromaticity of the rings exerts a negative interference effect on the conductance, as the electron transfer between electrodes comes with a loss of aromatic stabilization. However, for systems with pX2 like contacts, the aromaticity of the ring has a positive interference and benefits the electron transport. A straightforward way to predict the effect of the aromaticity on the electron conductance, based on the analysis of the polarized and neutral conjugated VB structures, has been proposed.

In addition, a study of the effect of the chain length in the conductance was performed. Using the pP linker, a linear relation between conductance and the inverse of the chain length was found similar to macroscopic wires. However, using the pX2 linker, the conductance is reinforced with the length of the chain when the aromaticity of the ring units reaches a significant value. These trends can be explained in terms of the balance between chain length and electronic effects in each case. For the pX<sub>2</sub> linker, the large increase of the aromaticity with the number of ring units comes with an important electronic stabilization of the system, rising its electric conductivity ( $\sigma$ ) and overcoming the expected conductance decrease inherent to a lengthening of the chain. In the pP linker, the changes in the aromaticity with the number of ring units are almost negligible, therefore, only the effect of the chain length can be seen.

#### Acknowledgements

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