Atomic Charges, Molecular Orbital Analysis and Effect of Metal Electrodes on 1, 2-di (biphenyl-4-yl) Ethyne Molecular Nanowire by Quantum Chemical Calculations

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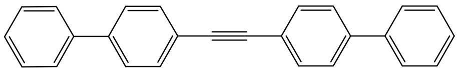
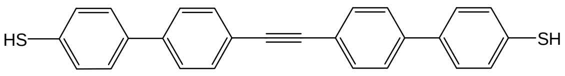
Abstract: ***The atomic charges and molecular orbital analysis of 1, 2-di (biphenyl-4-yl)ethyne molecule has been studied by using quantum chemical calculations. The entire study has been carried out with density functional theory (DFT) coupled with Bader's theory of atoms in molecules using Gaussian09 program package. The molecule has been analyzed by substituting thiol, Au and Pt atoms with both ends of the free molecule, in which thiol atoms acts as linker whereas Au and Pt atoms act as electrodes. Atomic charges of the free molecule as well as all the substituted molecules have been compared with MPA and NPA charges. The HOMO-LUMO gap (HLG) of the free molecule, S, Au and Pt substituted molecules are found to be 3.92, 3.73, 2.20 and 0.08 eV respectively. The existence of small HLG of Au or Pt substituted molecules enhances the conductivity.***

1. Introduction

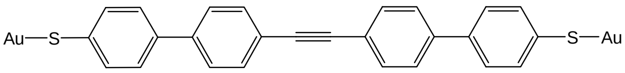
In the Recent years, molecular electron transfer is one of the most basic chemical processes, which has been an active field of nano research. Molecular electronics is a field whose progress depends on improved techniques for design and optimization of conducting structures at the atomic level [1-3]. Organic molecules with extended π−conjugated systems are of considerable current interest in molecular electronics due to their potential applications in nano electronic devices [4]. Conjugated molecules, comprise of alternate single and double (or triple) carbon–carbon bonds, can conduct electrons have been the basis of many molecular wires [4,5]. Hence, construction of a molecular wire normally requires the conjugated electronic structure of an elongated molecule through which electrons can readily flow from one end to the other. In other words, a conjugated system provides a pathway where electron clouds overlap between molecular components so that electrons can hop from one to another [6]. Several types of molecules have been suggested as molecular wires so far, they all have the same key requirements. Designing and synthesizing of enhanced molecular wires may be facilitated by theoretical techniques with more reliable predictive capabilities. Quantum chemical calculations using Density functional theory with no adjustable parameters introduced for the purpose of obtaining agreement with existing experimental data can be expected to provide innovative insights into experiments and to make useful predictions on new molecular wires [6,7]. In the present study, we report the theoretical and computational achievements of atomic charges and molecular orbital analysis on 1, 2-di (biphenyl-4-yl)ethyne molecular nanowire. The 1, 2-di (biphenyl-4-yl)ethyne (Free molecule / molecule-I) has been attached with Au or Pt atoms at both ends through thiol atom in which, Au or Pt atoms act as metal electrodes for applying external electric field where as thiol atom act as good linker between the molecule and metal electrodes. The thiol, Au and Pt substituted 1, 2-di (biphenyl-4-yl)ethyne molecules (molecule-II, molecule-III and molecule-IV) are shown in fig.1



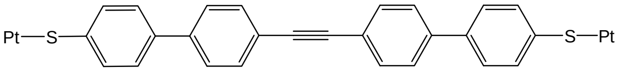
molecule -I (free molecule)



molecule-II (substituted with S)



molecule-III (substituted with Au)



molecule-IV (substituted with Pt)

Figure 1: 1, 2-di (biphenyl-4-yl)ethyne molecule with various substitutions

2. Computational Details

In the present investigation, all the Density Functional Theory (DFT) calculations were carried out using Gaussian 09 program [8] coupled with Bader's quantum theory of atoms in molecules. Full geometry optimization using DFT has been carried out using Becke's three parameter hybrid function with Lee-Yan-Parr correlation function (B3LYP) [9] and an effective core potential basis set LANL2DZ (Los Alamos set of double-zeta) [10-13] for metal electrodes. Fig.2 shows the optimized geometry of the free as well as substituted molecules. The quantum chemical calculations have been carried out using GaussView program. The GaussSum program has been used to determine the density of states (DOS) of all the molecules [14].

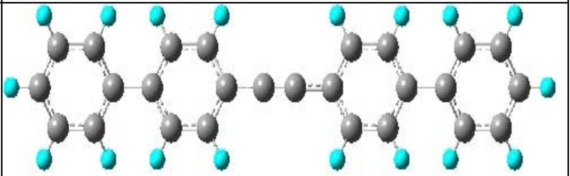
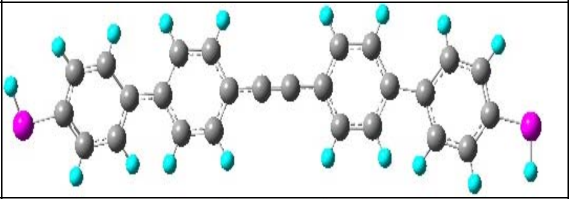
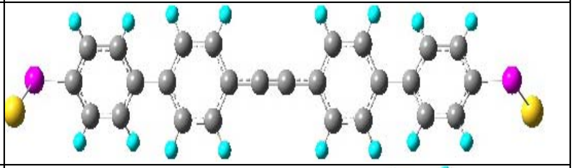
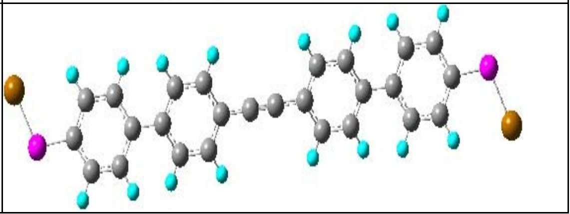
Molecule	*Optimized geometry*
I	
II	
III	
IV	

Figure 2: Optimized geometry of I-free molecule, II-substituted with S, III- substituted with S and Au, and IV-substituted with S and Pt.

3. Atomic Charges

Atomic charges for a given compound can be derived in multiple ways with a high level of convergence to the same values and only then, knowing the remaining uncertainty, are suited for molecular simulations. Mulliken charges arise from the Mulliken population analysis [15,16] and provide a means of estimating partial atomic charges from calculations carried out by the methods of computational chemistry. Specifically, these quantum chemical calculations mainly based on the linear combination of atomic orbital's molecular orbital method, and are routinely used as variables in linear regression [17] procedures. In the present work, the atomic charges have been estimated from Milliken population analysis (MPA) as well as natural population analysis (NPA) methods.

The MPA charges of all C-atoms for all the four kinds of molecules vary from -0.037 to 0.415e. The linker atoms on either ends [S(1) and S(2)] possess same MPA charge for molecule-II (0.038e), molecule-III (0.084e) and molecule-IV (0.095e). The charges of Au atom at both ends of the molecule-III are equal (-0.054e). Similarly, the charges of Pt atom at both ends of the molecule-IV are equal (-0.213e). The MPA charges for all the four kinds of molecules are presented in Table. 1. The variations of MPA charges for the molecules-II, III and IV with reference to molecule-I are plotted as in Fig.3.

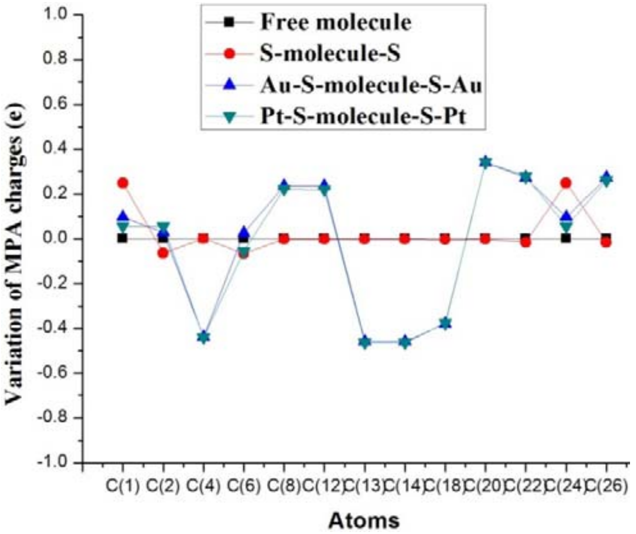


Figure 3: Variation of MPA charges of the molecules-II, III and IV with reference to molecule-I.

Table. 1 MPA Atomic charges (e) of the molecules

Atoms	I	II	III	IV	Atoms	I	II	III	IV
C(1)	-0.126	-0.376	-0.222	-0.181	C(17)	-0.141	-0.140	-0.378	-0.361
C(2)	-0.172	-0.108	-0.201	-0.228	C(18)	-0.040	-0.037	0.340	0.337
C(3)	-0.103	-0.087	-0.377	-0.364	C(19)	-0.141	-0.140	-0.378	-0.363
C(4)	-0.080	-0.081	0.359	0.361	C(20)	-0.064	-0.063	-0.406	-0.406
C(5)	-0.103	-0.087	-0.376	-0.382	C(21)	-0.080	-0.081	0.359	0.361
C(6)	-0.172	-0.106	-0.197	-0.117	C(22)	-0.103	-0.087	-0.377	-0.382
C(7)	-0.040	-0.037	0.340	0.337	C(23)	-0.172	-0.106	-0.201	-0.117
C(8)	-0.141	-0.140	-0.378	-0.363	C(24)	-0.126	-0.376	-0.222	-0.181
C(9)	-0.064	-0.063	-0.406	-0.406	C(25)	-0.172	-0.108	-0.197	-0.228
C(10)	0.320	0.322	0.412	0.415	C(26)	-0.103	-0.087	-0.376	-0.364
C(11)	-0.064	-0.064	-0.406	-0.407	S(1)	—	0.038	0.084	0.095
C(12)	-0.141	-0.140	-0.378	-0.361	S(2)	—	0.038	0.084	0.095
C(13)	-0.570	-0.569	-0.112	-0.106	Au(1)	—	—	-0.054	—
C(14)	-0.570	-0.569	-0.112	-0.106	Au(2)	—	—	-0.054	—
C(15)	0.320	0.322	0.412	0.415	Pt(1)	—	—	—	-0.213
C(16)	-0.064	-0.064	-0.406	-0.407	Pt(2)	—	—	—	-0.213

The NPA charges of all C-atoms for all the four kinds of molecules vary from -0.002 to 0.011e. The linker atoms on either ends [S(1) and S(2)] possess same NPA charge of molecule-II (-0.064e), molecule-III (-0.149e) and molecule-IV (0.074e). The charges of Au atom at both ends of the molecule-III are equal (0.217e). Similarly, the charges of Pt atom at both ends of the molecule-IV are equal (-0.071e). On the whole, it is found to be MPA and NPA charges of linker thiol atoms gradually increases for substituting Au and Pt metal electrodes. The NPA charge distribution for all the molecules are listed in Table 2. The variations of NPA charges for the molecules-II, III and IV with reference to molecule-I are plotted as in Fig.4.

Table 2: NPA Atomic charges (e) of the molecules

Atoms	I	II	III	IV	Atoms	I	II	III	IV
C(1)	-0.201	-0.121	-0.165	-0.171	C(17)	-0.192	-0.190	-0.200	-0.195
C(2)	-0.193	-0.204	-0.196	-0.201	C(18)	-0.037	-0.040	-0.042	-0.035
C(3)	-0.192	-0.183	-0.200	-0.194	C(19)	-0.192	-0.190	-0.200	-0.195
C(4)	-0.047	-0.040	-0.035	-0.033	C(20)	-0.156	-0.155	-0.168	-0.164
C(5)	-0.192	-0.184	-0.200	-0.191	C(21)	-0.047	-0.040	-0.035	-0.033
C(6)	-0.193	-0.205	-0.196	-0.192	C(22)	-0.192	-0.184	-0.200	-0.191
C(7)	-0.037	-0.040	-0.042	-0.035	C(23)	-0.193	-0.205	-0.196	-0.192
C(8)	-0.192	-0.190	-0.200	-0.195	C(24)	-0.201	-0.121	-0.165	-0.171
C(9)	-0.156	-0.155	-0.168	-0.164	C(25)	-0.193	-0.204	-0.196	-0.201
C(10)	-0.121	-0.119	-0.105	-0.101	C(26)	-0.192	-0.183	-0.200	-0.194
C(11)	-0.156	-0.155	-0.168	-0.164	S(1)	—	-0.064	-0.149	0.074
C(12)	-0.192	-0.190	-0.200	-0.195	S(2)	—	-0.064	-0.149	0.074
C(13)	0.010	0.011	-0.002	0.008	Au(1)	—	—	0.217	—
C(14)	0.010	0.011	-0.002	0.008	Au(2)	—	—	0.217	—
C(15)	-0.121	-0.119	-0.105	-0.101	Pt(1)	—	—	—	-0.071
C(16)	-0.156	-0.155	-0.168	-0.164	Pt(2)	—	—	—	-0.071

4. Molecular Orbital Analysis

Molecular orbitals are obtained from the combination of atomic orbitals, which predict the location of an electron in an atom. A molecular orbital is a mathematical function describing the wave-like behavior of an electron in a molecule [18,19]. This function can be used to calculate the chemical and physical properties such as the probability of finding an electron in any specific region [19,20]. The most important orbitals in molecules for reactivity are the two so called frontier orbitals known as HOMO and LUMO. HOMO is the highest occupied molecular orbital and LUMO is the lowest unoccupied molecular orbital [21]. The energy difference between the HOMO and LUMO is termed as the HOMO–LUMO gap (HLG). The charge transport properties [22] of the molecule mainly depends on HLG, hence, it is necessary to examine the variations in HLG and molecular orbital energy levels. Fig.5 illustrates the energy levels of all the molecules calculated from quantum chemical calculations.

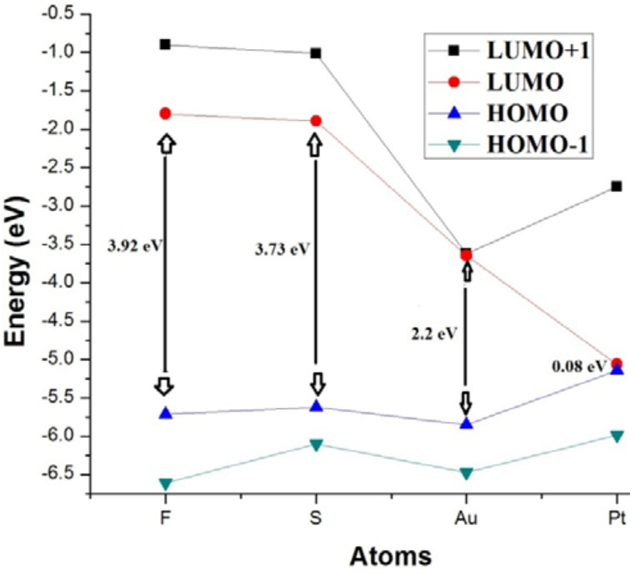
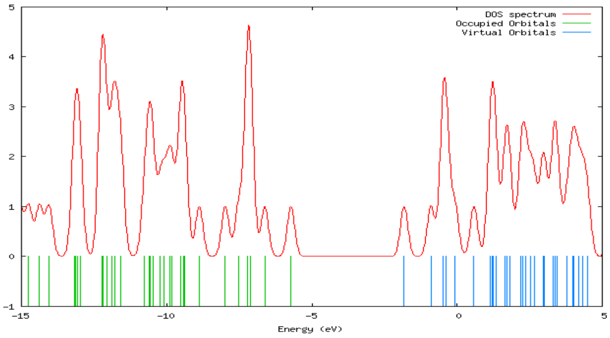
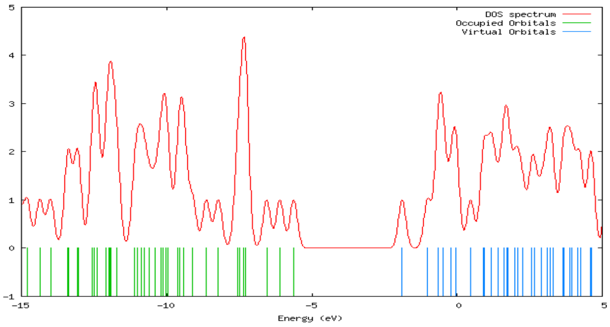


Figure 5: Energy level diagram of free molecule (F), S, Au and Pt substituted molecules

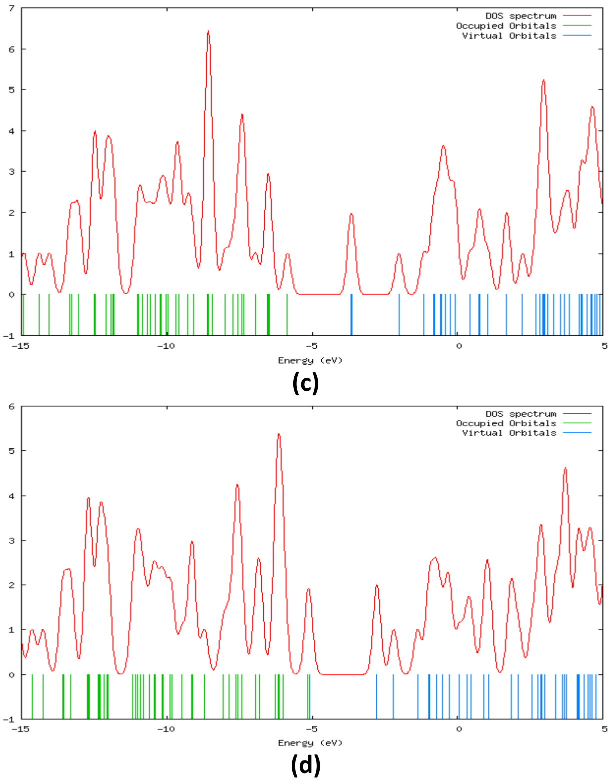
The HLG can also be determined from the density of states (DOS) spectrum [23]. DOS of a system describes the number of states per interval of energy at each energy level that are available to be occupied by electrons. A high DOS at a specific energy level means that there are many states available for occupation. A DOS of zero means that no states can be occupied at that energy level [24]. Fig.6 [(a)-(d)], shows the density of states (DOS) for the molecules- I, II, III and IV in which the green lines indicate the HOMO and the blue is LUMO, the decrease of HLG is also shown. Here, the hybridization of the molecular level with that of the gold atom broadens the DOS peaks. The HLG of molecules-I, II, III and IV are 3.92, 3.73, 2.20 and 0.08 eV respectively. The large decrease of HLG of the molecule-III and molecule-IV facilitates large electron conduction through the molecule [7], hence, the Au or Pt substituted molecule can act as an efficient molecular nanowire.



(a)



(b)



(c)

(d)

Figure 6: [(a)-(d)], Shows the density of states (DOS) for the molecules-I, II, III and IV.

5. Conclusion

The present computational study on 1, 2-di (biphenyl-4-yl)ethyne molecular nanowire describes the difference in atomic charges of the molecule substituted with thiol, Au and Pt atoms. The linker thiol atoms on either ends [S(1) and S(2)] possess same MPA charge for molecule-II (0.038e), molecule-III (0.084e) and molecule-IV (0.095e). The charges of Au atom at both ends of the molecule-III are equal (-0.054e). Similarly, the charges of Pt atom at both ends of the molecule-IV are equal (-0.213e). Similarly, the NPA charges of thiol, Au and Pt atoms at both ends of the molecules are equal; however, there is slight difference between MPA and NPA charges of all atoms. Further, it is found to be MPA and NPA charges of linker thiol atoms gradually increases for substituting Au and Pt metal electrodes. From the DOS spectrum, the HLG of molecules-I, II, III and IV are found to be 3.92, 3.73, 2.20 and 0.08 eV respectively. The large decrease of HLG of the molecule-III and molecule-IV facilitates large electron conduction through these molecules, hence, charge transport increases for the Au or Pt substituted molecules. However, Au electrodes are user friendly than Pt electrodes, hence, 1, 2-di (biphenyl-4-yl)ethyne molecule using Au as electrodes with thiol as linker can act as efficient molecular nanowire.

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