

## Theoretical Study of Substituent Effect of Physical Properties and Conductivity of Cyclo(12)thiophene

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### Abstract

The optimized geometries and energy bands ( $E_g$ ) for neutral and protonated of 3-substituted-cyclo(12)thiophene (X-CT<sub>12</sub>) have been obtained by using the semi-empirical method at level PM3, the substituents were, H, CH<sub>3</sub>, OCH<sub>3</sub>, NMe<sub>2</sub>, Cl, CN and NO<sub>2</sub>. The  $E_g$  for protonated oligothiophenes all fall about 2 eV comparing with neutral ones. The substituent effect on molecular orbitals HOMO and LUMO were significant.

**Keywords:** Substituent effects, HOMO and LUMO, Conductivity.

### Introduction

Polythiophenes and their finite model oligomers,  $\alpha$ -conjugated oligothiophenes, belong to the most thoroughly investigated  $\pi$ -conjugated systems in the field of material science [1,2]. Due to their chemical stabilities in their various redox forms and their outstanding structural and electronic properties, they are potential candidates for applications in molecular electronic devices such as organic field-effect transistors [ 3-9 ], light-emitting devices, [10,11] photovoltaic cell[12] or even as molecular wires for information storage or transfer[13-17] . The systematic investigations of well-defined oligothiophenes provide valuable information about the structure-property relationship of these compounds and by correlation of their corresponding polymers. Such correlations are essential prerequisites for a molecular design and engineering of material properties.

In general, the physical properties of oligomers well-defined  $\pi$ -conjugated chain length are influenced by undesired perturbing end-effects[18].

In this respect, much more appealing seems to be molecules with a well-defined cyclic structure. Over the usual linear conjugated oligomers and polymers, the cyclic compounds have the distinct advantage, to ideally combine an infinite defect-free  $\pi$ -conjugated chain of an idealized polymer with the structural feature of a well-defined oligomer, but excluding perturbing end-effects. The fully  $\pi$ -conjugated macrocycles, which are designated as **cyclo(*n*)thiophenes** (*n* = number of thiophene rings), represent a novel class of shape-persistent nanosized macrocycles with particularly appealing characteristics and perspectives [19]. A recent study[20] has been investigated the substituent effect on the conductivity of the ground and excited states of the substituted oligothiophene (X-T<sub>14</sub>) and their cation radicals (T<sub>14</sub><sup>+</sup>). The aim of this study is to investigate the substituent effect on the physicals properties and conductivity of the 3-substituted cyclo(12)thiophene Fig. 1.

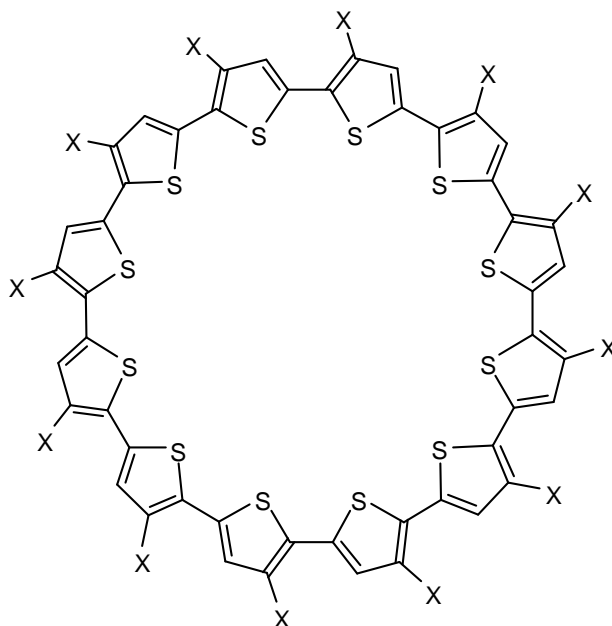


Fig. 1: Structure of 3-substituted-cyclo(12)thiophene

### ***THEORETICAL APPROACH***

Geometry optimizations were carried out the PM3 [21] semiempirical methods as implemented in the Hyperchem 7.5 package. All structures were fully optimized at the Restricted Hartree – Fock (RHF) [22] formalism which is sufficient for studying the

system considered in this work. Geometry optimizations were carried out by using a conjugate gradient method (Polka – Ribiere algorithm) [23] . The self-consistent-field SCF convergence was set to 0.01 Kcal mol<sup>-1</sup> in the calculations.

### **Results and Discussion**

Some molecular information, total (T.E), binding (B.E) and electronic energy (E.E), heat of formation ( $\Delta H_f$ ), HOMO, LUMO and energy gap  $E_g$  for the 3-substituted cyclo(12)thiophene X-CT<sub>12</sub> and protonated 3-substituted cyclo(12)thiophene X-CT<sub>12</sub><sup>+</sup> systems considered are given in Table 1 and 2 respectively.

#### **Before Protonated**

The heat of formation ( $\Delta H_f$ ) of all compounds are endothermic especially with CN substituent (899 kcal/mol). The effect of substituent X on the  $\Delta H_f$  was decreasing it comparing with unsubstituted one

except in (X = CN and OCH<sub>3</sub>) which were (899 kcal/mole and 506 kcal/mole) respectively.

The effect of substituent X on total (T.E), binding (B.E) and electronic (E.E) energies were generally larger than unsubstituted compound.

#### **After Protonated**

The comparison between Table 1 and 2, one can observed that there is no significant effect of protonation (doping) on the total energy, binding energies, and electronic energy, this means that the oligomers kept its stability after doping. The heat of formation largely increased.

**The Conductivity ( $E_g$ )**

From the comparison between two molecular orbitals energy columns before and after doping (Table 1 and 2), it can be seen, that the doping generally, diminishes (stabilizes) the HOMO energies about  $\approx 1$  eV, whereas it diminishes the LUMO energies about  $\approx 4$  eV.

The falling of  $E_g$  above 3 eV (i.e. out of semiconductive region) do not make these 3-substituted cyclo(12)thiophenes act as a semiconductor comparing with substituted oligothiophenes this may attribute to that the latter has an charged edges which play important role in conductivity as a dipoles whereas the 3-substituted cyclo(12)thiophenes is not.

The qualitative relationships between the frontier orbitals and the electronic parameters of substituents X have been studied. The calculations of the orbital energies of 3-substituted cyclo(12)thiophenes (X-

CT<sub>12</sub><sup>+</sup>) show a systematic lowering of both the HOMO and LUMO energies. In (Fig.2) a and c shows that a reasonable linearity observed ( $r = 0.860$ ,  $r$ : correlation

coefficient) between HOMO and the Hammett  $\sigma_p$  constants, whereas it was ( $r = 0.873$ ) between LUMO and the Hammett  $\sigma_p$  constants. The substituent X=NMe<sub>2</sub> deviate from this linearity in both relationship this because the strong donating substituent make the structure of oligothiophene non-planar which cause reducing the transfer of the field and resonance effect along the cyclic aromatic system. If the X=NMe<sub>2</sub> excluded the relationship would be more linearity for both HOMO and LUMO ( $r = 0.961$  and  $0.984$ ) respectively as shown in (Fig.2) b and d.

**Table (1) : total, binding and electronic energy, heat of formation, HOMO, LUMO and energy gap  $E_g$  for X-CT<sub>12</sub>**

sub	HOMO	LUMO	$E_g$	$\Delta H_f$	B.E	E.E	T.E
H	-8.193	-1.854	6.338	434	-9815	-2044904	-190942
CH <sub>3</sub>	-8.191	-1.538	6.653	370	-9602	-2975080	-274335
OCH <sub>3</sub>	-8.050	-1.483	6.567	506	-14260	-4055722	-313473
NMe <sub>2</sub>	-8.254	-1.542	6.712	413	-18420	-5240639	-322813
Cl	-8.474	-2.089	6.385	370	-9602	-2975291	-274335
CN	-9.698	-2.852	6.846	899	-12142	-3266584	-264048
NO <sub>2</sub>	-10.202	-6.605	6.595	399	-12011	-4944154	-393277

**Table (2) : total, binding and electronic energy, heat of formation, HOMO, LUMO and energy gap  $E_g$  for X-CT<sub>12</sub><sup>+</sup>**

sub	HOMO	LUMO	$E_g$	$\Delta H_f$	B.E	E.E	T.E
H	-9.567	-5.505	4.062	604	-9697	-2057764	-191126
CH <sub>3</sub>	-9.456	-5.253	4.203	488	-13115	-2972806	-232559
OCH <sub>3</sub>	-9.328	-4.957	4.371	169	-14148	-4079695	-313663
NMe <sub>2</sub>	-9.395	-5.245	4.150	579	-18306	-5259648	-323001
Cl	-9.753	-5.626	4.127	543	-9480	-2990954	-274515
CN	-10.906	-6.584	4.322	1084	-11999	-3281749	-264207
NO <sub>2</sub>	-11.564	-7.009	4.555	605	-11856	-4958387	-393424

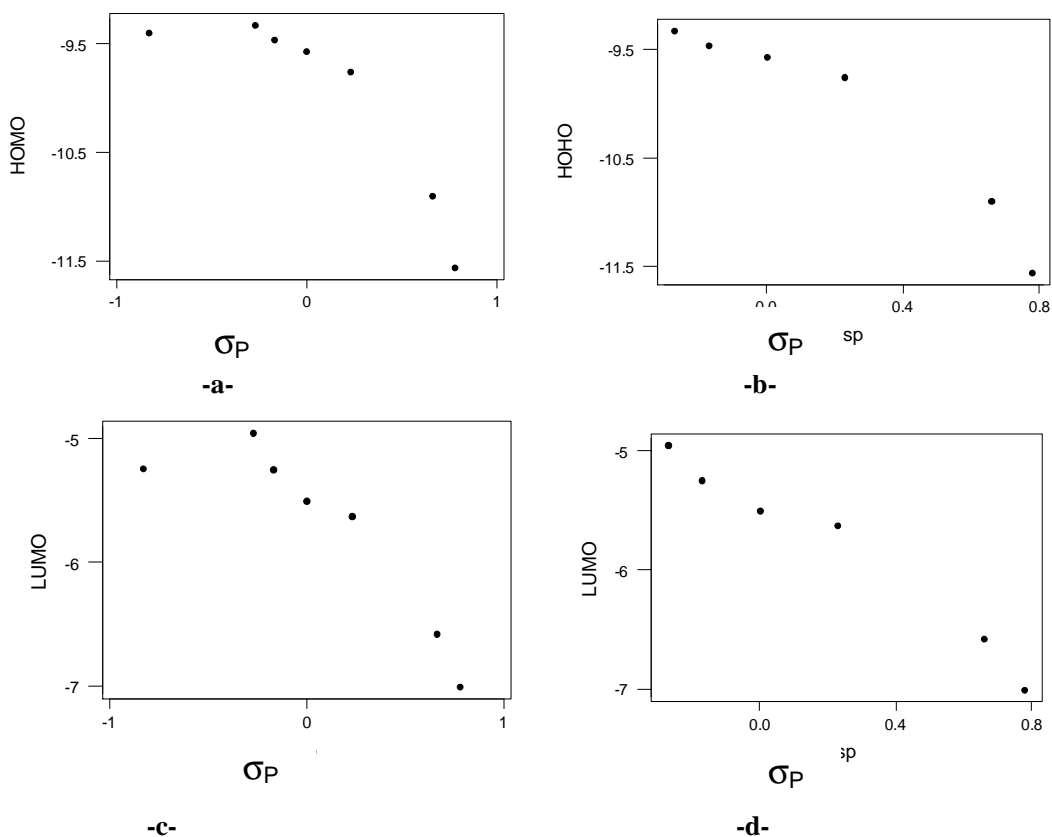


Fig. (2) : The relationship between  $\sigma_P$  of Hammett and Molecular Orbitals (HOMO and LUMO of series X-CT<sub>12</sub><sup>+</sup>)

a) with HOMO before exclude  $\text{NMe}_2$     b) with HOMO after exclude  $\text{NMe}_2$   
 c) with LUMO before exclude  $\text{NMe}_2$     d) with LUMO after exclude  $\text{NMe}_2$

### Conclusion:

It can be concluded from data of optimized geometries and energy bands ( $E_g$ ) for neutral and protonated of 3-substituted- cyclo(12)thiophen (X-CT<sub>12</sub>), the protonation increased conductivity of

compounds under investigation. The constituent effect were clear on conductivity of protonated oligothiophenes, the effect were significant on molecular orbitals HOMO and LUMO.

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### الخلاصة

تم في هذه الدراسة حساب قيم فرق الطاقة ( $E_g$ ) لمركبات X-CT<sub>12</sub> 3-substituted-cyclo(12)thiophene المعوضة بصيغتيه المتعادلة والمبرتنة باستخدام طريقة PM3 الشبه تجريبية حيث ان (H, CH<sub>3</sub>, OCH<sub>3</sub>, NMe<sub>2</sub>, Cl, CN and NO<sub>2</sub> = X). من خلال النتائج وجد بان قيم فرق الطاقة لجميع المركبات المبرتنة اقل بحوالي 2 الكترون فولت مقارنة بالمركبات المتعادلة. كما وجد بان تاثير المعوض كان معنوياً على الاوربتالات الجزيئية HOMO و LUMO.