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Neutral and doped oligofurans as low gap organic materials, electronic and absorption properties

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ABSTRACT

The Polyfuran belong to an important class of conjugated systems whose electronic properties strongly improve under doping. In the present paper, theoretical analysis of the molecules of oligofurans has been reported. The methodology adopted is based on DFT (B3LYP/ 6-31(G) (d) calculations. The electronic, electrochemical and absorption properties were determined for the studied compounds. Strong agreement between estimated properties and available experimental data sustains use of this computational method.

Keywords: Oligofurans, π -Conjugated oligomers, DFT, electronic properties, Gap energy.

INTRODUCTION

The development of new organic semi-conductors, which is based on π -conjugated polymers, constitute an interesting and desirable domain in consequence to obtain materials with interesting optical, nonlinear optics and electrical conduction properties for electronic and photovoltaic applications [1-4], but also having enhanced fluorescence, solubility, and rigidity.

Polyfuran is one of the most studied π -conjugated polymers, his monomer is one of the five-membered heterocycles such as polythiophene and polypyrrole, its interesting properties emphasizes this polymer more and more for new applications: as anticorrosion coating or antistatic wrapping materials, in capacitors rechargeable secondary batteries catalysts conducting polymer-grafted carbon materials for fuel cell applications and electrically conducting lubricating greases for electric motors, also for the conversion of solar energy in photovoltaic cells. Generally, the furan aromatic character is weak, that is proved by his good reactivity in the Diels-Alder reactions⁵, also the fort ring fragility which is easily opened in acid environment or by photo-oxidation in the presence of O₂. The weak aromaticity compared with thiophene and pyrrole permit excellent π -electrons delocalization through conjugated chain [5]. In fact, the two π - electrons offered by the heteroatom plus the four π - electrons from the carbon atoms, provide aromatic system. Therefore, the electrical and optical properties of these polymers are highly influenced by the augmentation electro-negativity of the heteroatom.

In this work, the theoretical investigation on studying oligofurans (nfu) has certainly provided in detail peculiarities that allow get around the problems about understanding the mechanisms which control the charge transport in parent polymers [6]. In this regard, theoretical studies of the physical and structural properties of oligofurans permit the

knowledge of polymer structure and contribute to the experiment information to rationalize the coupling between the structure and the geometry when properties of study compound are associated mostly to the π -electrons.

Thus, we are going to carry out the DFT calculations and to discuss the structural and electronic properties of neutral and doped oligofurans. The results of neutral and doped states are discussed in comparison with the properties of others five-membered heterocyclic. We are particularly interested in the effect of π -conjugated chain length on structural and electronic properties of the studying molecules in order to make accurate comparisons of the calculated values of HOMO, LUMO and Gap energies with experiment.

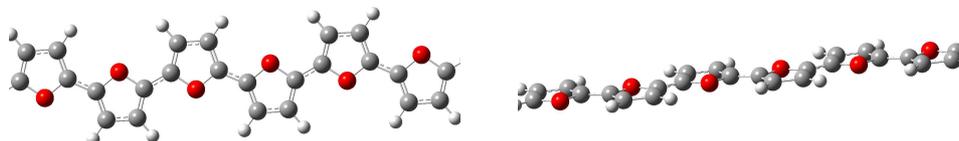


Figure.1: Structure of polyfuran

Computations:

All calculations were performed using ab-initio DFT method. The geometries of study molecules were optimized by the B3LYP hybrid functional with the basis sets (6-31G(d)). The B3LYP level constitutes the most used methods in DFT theory, it provides the smaller value of average error (2.5 kcal/mol) among results have been shown by quantum approaches as Diffusion Monte Carlo (2.9 kcal/mol) or Coupled Cluster Approximation (2.8 kcal/mol) [7]. We have also studied absorption by the semi-empirical ZINDO and TD-DFT calculations which generate the transition energies and oscillator strength, no empirical corrections were incorporated into the estimation of transition energies. In fact, these calculation methods are useful to aid in the design of materials and have been intensively applied to other conjugated polymer [8-9]. Also, we have successfully used the DFT method to predict properties of Polypyrrole and some Pyrrole derivatives suggested for organic solar cell applications [10]. All calculations were carried out using the GAUSSIAN 03 program [11] using molecular structure as the only input required.

Geometric properties:

The DFT calculations were performed on the structure of oligofurans with the purpose to take out the necessary information in order to find the corresponding geometric form in each state, such a way that the numerical values can be compared throughout the series of molecules (Table 1). We can expect an aromatic behaviour provided that the structure is planned and electrons number respects the Hückel rule permitting delocalization. In other hand, according to Hernandez and *al.* [12] the nearest neighbours submit interaction force constants, and rapidly decrease with the distance of interaction increasing. Concerning the polymer PFu, his skeleton presents an anti conformation in solid state at low temperature. Moreover, the long molecular chains of PFu can be regarded as a one dimensional crystal when intra-molecular forces are strong compared with the inter-molecular ones [13].

Table 1: Inter-ring distances d_i (Å) of study compounds obtained by B3LYP/6-31G(d) calculations

Inter-ring distances Å)	d_1	d_2	d_3	d_4	d_5	d_6
7Fu	1.43446	1.43072	1.43016	1.43016	1.43072	1.43446
6Fu	1.43449	1.43078	1.43034	1.43078	1.43449	-
5Fu	1.43449	1.43087	1.43087	1.43448	-	-
4Fu	1.43459	1.43143	1.43458	-	-	-
3Fu	1.43508	1.43508	-	-	-	-
2Fu	1.43830	-	-	-	-	-

We theoretical study the effect of doping in the sixth oligomer (6Fu) with the level UB3LYP 6-31G (d)). Our attention was focused on the study of the geometrical properties in neutral with doped states: the polaron (radical cation 6Fu^+) and bipolaron (dication 6Fu^{++}).

When we compare the inter-ring bond for 6Fu in the neutral and doped states, values (Table 2) show that the contribution from the quinoid structure is very weak in neutral states, however appears strongly in polaronic and bipolaronic cases.

Figure. 2: The neutral (a), polaron (b) and bipolaron states for the sixth oligomer (6Fu)

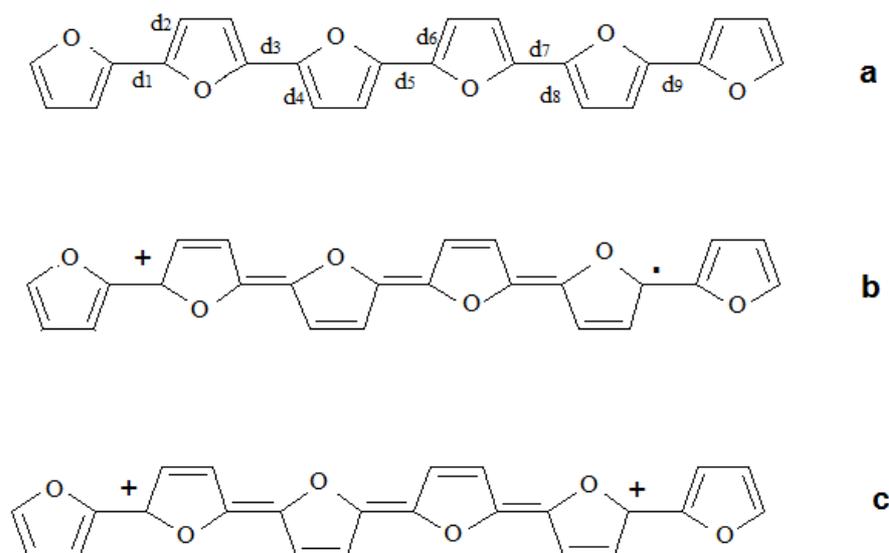


Table 2: Geometric parameters of 6Fu oligomer obtained by B3LYP/6-31G(d) in their neutral and doped (polaronic and bipolaronic)

Inter-ring distances (Å)	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	d ₇	d ₈	d ₉
Neutral (a)	1.434	1.374	1.431	1.375	1.430	1.375	1.431	1.374	1.434
Polaron (b)	1.421	1.390	1.408	1.396	1.405	1.396	1.408	1.390	1.421
Bipolaron (c)	1.403	1.411	1.387	1.418	1.384	1.417	1.387	1.409	1.403

Within the context of molecular electronics, studies on the structure of charge oligofurans are associated with Holt moving through single molecule; this effect can be produced from the p-doping process on the semi-conducting molecule. For example, structural parameters of the 6Fu in its quinoidic form (polaronic and bipolaronic) indicate that the cycles at the ends preserve their aromatic character, whereas the central processing units present a quinoid character. This is summarized on Fig.3.

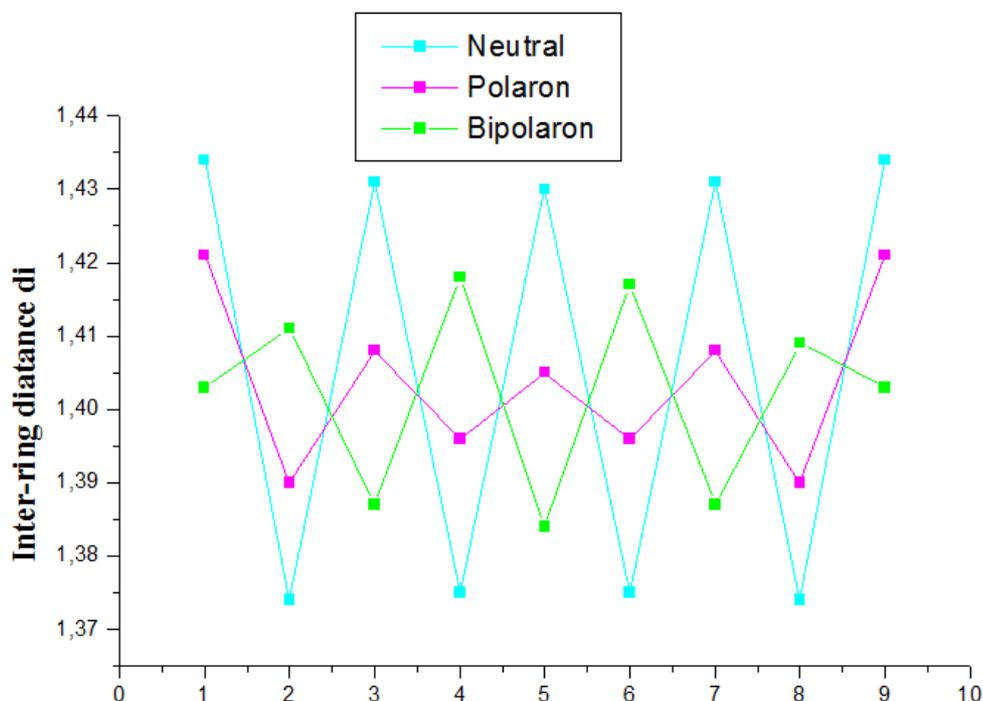


Figure.3 : Optimized C-C bond lengths of neutral(a) and doped(polaron (b), bipolaron (c)) states of the sixth oligofuran (6Fu)

Electronic and optical properties

After the Kohn-Sham theory, the bands become actually an important physical entities to describe the electron system energies, it is clear that the electronic properties are strongly depends upon the structure of bands, consequently we need the band gap width (E_g) as central quantity in molecular orbital theory. This quantity presents one of the most important factors of controlling electrical and optical properties, in that way materials with a low band gap constitute desirable compounds for several uses especially in optical and electronic fields [14]. Some authors have also studied the electronic properties of Polyfuran, among these studies, we can cite the work of Glenis and *al.* [15] who synthesized polyfuran films and an important investigation was carried out.

Theoretically, we found HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) levels using DFT calculation upon optimized structures of all oligomers nFu. Extrapolation of the HOMO, LUMO and gap calculated energy values of oligofurans against $(1/n)$ the reciprocal of the number of monomer units shows a linear correlation (Figure 4). Therefore, we obtain -4.27, -1.93 and 2.33 eV which correspond respectively to the theoretical HOMO, LUMO and gap energies for the Polyfuran. These results prove that this way constitute a good approximation to characterize the Polymer parent.

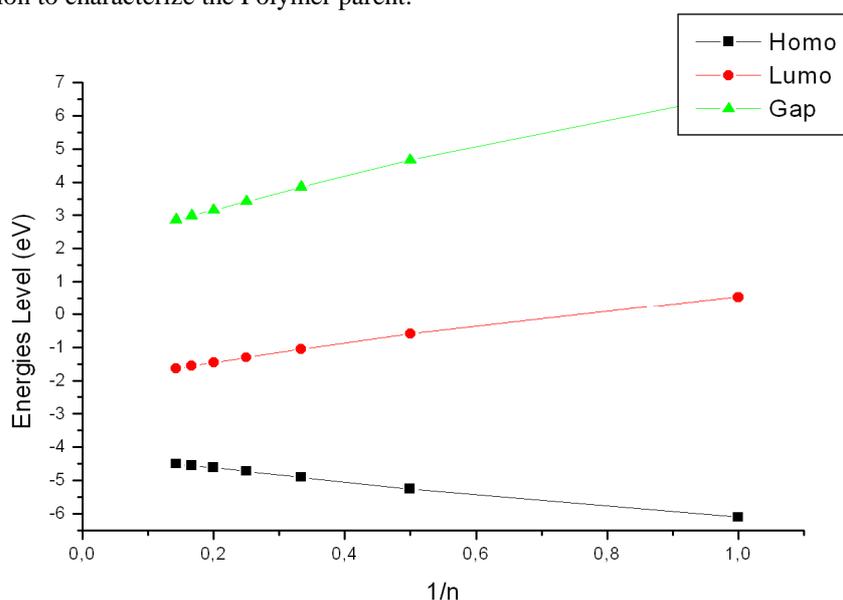


Figure.4: Calculated HOMO, LUMO and Gap energies and the reciprocal of the number of oligomer [B3LYP/6-31G(d)]

In Table 3, we list the theoretical electronic parameters of the studied oligomers. Generally, the Ionization Potential (IP) is evaluated as the difference between the ground state of the cation (nFu^+) and the neutral molecule S_0 (nFu). However, the Electron Affinity (EA) is given by the difference between IP and the gap energy [16] as shown in Figure 5.

Figure.5: Schematic representation of band structure for semi-conducting materials

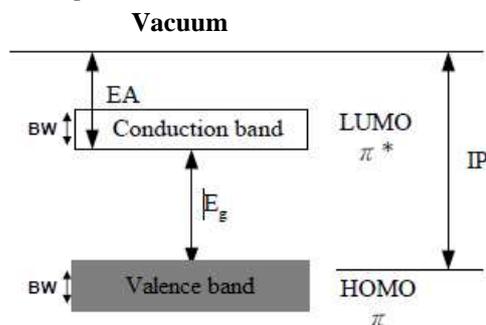


Table 3: Values of electronic properties the band gap width E_g (eV), Ionization Potential (eV) and Electron Affinity (eV), calculated for the optimized structure of oligofurans, nFu (n=1-7)

Compounds	1Fu	2Fu	3Fu	4Fu	5Fu	6Fu	7Fu
Gap(eV)	6.647	4.665	3.853	3.421	3.160	2.987	2.871
IP(eV)	8.205	6.795	6.165	5.799	5.562	5.395	5.274
EA(eV)	1.558	2.130	2.311	2.378	2.401	2.408	2.403

The experiment shows that the HOMO and LUMO energies are estimated from an empirical formula based on the onset of the oxidation measured by cyclic Voltammetry [17]:

$$E_{HOMO} = -qE_{ox}(1.4 \pm 0.1) - (4.6 \pm 0.08) \text{ eV} \quad (\text{Equation.1})$$

In theory, the HOMO and LUMO energies can be calculated by the DFT calculation [18-19]. However, it is noticeable that solid-state packing effects are not included in the DFT calculations, which tend to affect the HOMO and LUMO energy levels in a thin film compared to an isolated molecule as considered in the calculations. Even if these calculated energy levels are not accurate, it is possible to use them to get information by comparing similar oligomers or polymers. Our interest focuses on the degree of agreement between the experimental and calculated physical properties of the Polyfuran.

In Table 4, we report the comparison between the experimental electrochemical properties and the calculated ones based on the optimized structures (B3LYP/6-31G(d)). For comparison, we present also the values of the gap energy of polymer in a neutral state. The calculations on the polymer are close to the experiments.

Table 4: Values of calculating electrochemical and electronic properties compared to the experimental results. (a) Experiment data from reference [15], (b) value deduced from Equation.1, (c) The optical band gap obtained from absorption spectrum by extrapolation of the plot $(Ah\nu)^2$ vs $h\nu$, (A absorption coefficient)

Properties	Experiment values	Calculated values B3LYP/6-31G(d)
Oxidation Potential (V/SCE)	0.20 ^(a)	0.15
HOMO (eV)	-4.32 ± 0.1 ^(b)	-4.27
LUMO (eV)	-2.15 ± 0.1 ^(b)	-1.93
Gap(eV)	2.35 ^{(a)(c)}	2.33

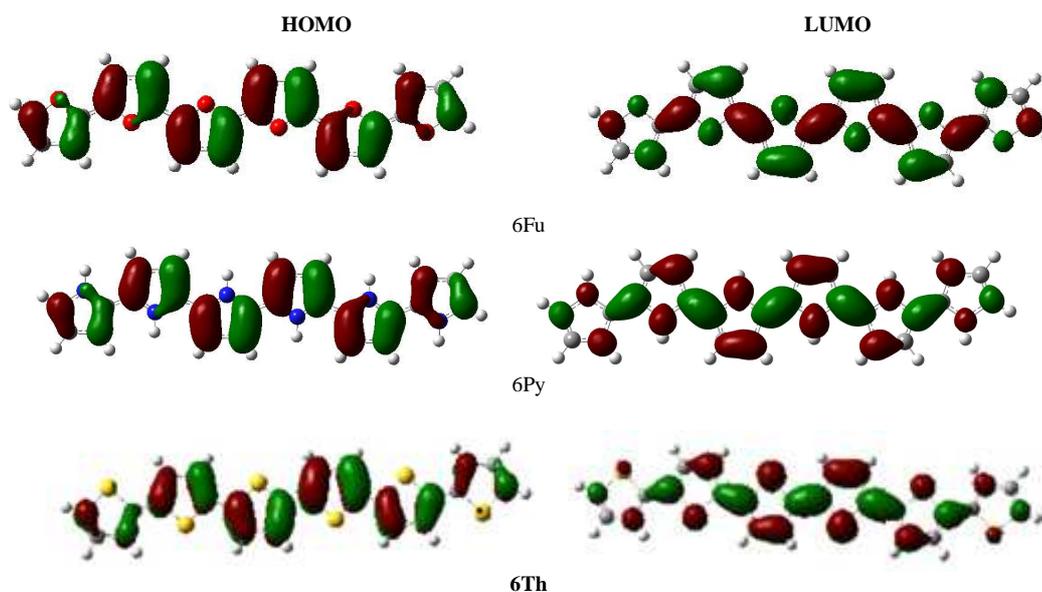


Figure.6: The contour plots of HOMO and LUMO orbital's of the sixth oligomers corresponding to Pyrrole, Furan and Thiophene

As well, the HOMO and LUMO energies examination is important because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitation properties. The Figure 6 shows the HOMOs of the three heterocyclic oligomers: Hexafurane (6Fu) Hexapyrrole (6Py) and Hexathiophene (6Th). These oligomers possess a π -bonding character within subunit and a π -antibonding character between the consecutive subunits. On the other hand, the LUMOs possess a π -antibonding character within subunit and a π -bonding character between the subunits.

The N and O atoms pull in electrons more than the S atom. Thus the last one allows electrons to be more delocalised along the chain. However, inter-ring delocalization is still allowed as can be drawn from the chain length dependence of geometric and electronic properties. The electro negativity of oxygen is the highest among others, thus compared with the thiophene and pyrrole, furan have the least resonance energy (16 kcal/mol) [20]. Also, the 6Fu possesses the greater molecular density (17% higher than in 6Th), although the molecular weight and size of 6Th are slightly larger than those of 6Fu [21].

The values of the gap energies are shown in Table 5 for 6Fu and 6Py oligomers in their neutral, polaronic and bipolaronic forms, respectively. We note that the energy gap decrease when passing from the neutral to the doped form for both molecules.

Table 5: Values of gap energy E_G (eV) calculated for 6Py¹⁰ (b) and 6Fu

State	6Fu	6Py
Neutral	2.98	3.36
Polaronic	2.66	3.07
Bipolaronic	1.26	1.06

The calculated electronic parameters (Gap, HOMO, LUMO) of compounds 6Py and 6Fu are (3.36eV, 2.98 eV), (-3.97 eV, -4.55 eV), and (-0.61eV, -1.56 eV) respectively in neutral form. The energy levels of compounds show that the pushing down HOMO and LUMO energies is in agreement with their character. However, 6Py has a smaller energy gap (E_G) than 6Fu, which is due to the highest electro-negativity of O atom. Furthermore, we can predict that Polyfuran can present middle properties between Polythiophene and Polypyrrole as a class of heteroaromatic conducting polymers.

In Table 5, we report the values of maximal absorption wavelength λ_{max} . The ZINDO method was used for calculations of transition energies and oscillator strengths and we start with optimized geometry obtained at B3LYP/6-31G(d) level. We note that calculations are performed under no constraints and in an isolated state, while the properties are measured in liquid state. In other hand, Matsuzawa and al [22-23] demonstrate that time-dependent density functional theory (TD-DFT) calculation gives successful results in the design of materials. This method has the particularity to reproduce the best λ_{max} values similar to those of the experience. The results are plotted in Figure 7.

Table 5: Calculated absorption λ_{max} (nm) and Oscillator Strength(O.S) for oligofurans (n=1,7) obtained by the ZINDO Method

Molecule	λ_{max} (nm) cal	O. S
1Fu	260.60	0.17
2Fu	352.45	0.56
3Fu	419.93	0.77
4Fu	466.67	1.02
5Fu	577.43	1.36
6Fu	524.26	1.52
7Fu	616.80	1.75

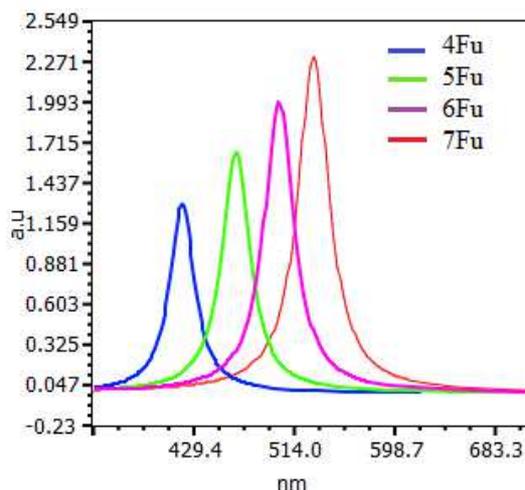


Figure.7: the absorption spectrum in a certain narrow range of UV- VIS region calculated at the TD-DFT level using 6-31G(d) basis set for the oligomers nFu (n=4 to 7)

The absorption wavelengths arising from $S_0 \rightarrow S_1$ electronic transition increase progressively with the increasing of conjugated chain lengths. Importantly, the maximal absorption shows a bathochromic shift when passing from small molecules to big ones, which also can be seen respectively in 4Fu (420 nm), 5Fu (465 nm), 6Fu (502 nm) and 7Fu (531 nm). The former data agrees with what is observed on experimental spectrum, where the broad absorption band of Polyfuran lies between 430 nm and 540 nm corresponding to the $\pi - \pi^*$ inter-band transition [15].

CONCLUSION

The DFT calculations at the level B3LYP were performed to investigate the geometric, electrochemical, electronic and optical properties of the Polyfuran with his oligomers (nFu). The molecular geometries indicate that quinoidic form is more pointed up since a second electron is removed to obtain bipolaron (nFu⁺⁺). The values of calculated gap energy with the same method have been decreased for each oligomer when it passes from the neutral to the doped forms. Further, the electrochemical and electronic properties can be well estimated from the calculated gap. The absorption spectrum in UV- VIS region is also calculated for the oligomers (nFu) using the ZINDO and TD-DFT methods, so we can deduce that results presented by the last method give the credible ones. Thus, our theoretical results for Polyfuran agree with the experimental data. Presumably, the efficient, low band gap allows furan-based polymers to be promising organic materials in electronic and optical application, also the oxygen-based conjugated materials constitute more biodegradable conducting compounds especially for solar cells compared to Sulfur or Selenium.

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