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ORIGINAL ARTICLE

DFT and quantum chemical investigation of molecular properties of substituted pyrrolidinones

Mohammed Bouklah [a], Houria Harek [b], Rachid Touzani [a,c,*], Belkheir Hammouti [a,], Yahia Harek [b]**

[a] *Laboratoire de Chimie Appliquée et Environnement, Département de Chimie (URAC 18), Faculté des Sciences, Mohammed 1er, BP: 717, 60 000 Oujda, Morocco*
[b] *Département de Chimie, Faculté des Sciences, Université Abou Bakr Belkaïd, 13000 Tlemcen, Algeria*
[c] *Faculté Pluridisciplinaire de Nador, Université Mohammed 1er, BP: 300, 6750 Selwane, Nador, Morocco*

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Abstract The DFT, quantum-chemical calculations and thermodynamics parameters of 1-{2-[(2-hydroxyethyl)thio]ethyl}pyrrolidin-2-one (HTEP); [2-(2-oxo-pyrrolidin-1-yl)-ethyl]-phosphonic acid diethyl ester (EOEP); {[2-(2-oxopyrrolidin-1-yl)ethyl]thio}acetic acid (OETA); (2-pyridin-4-yl-ethyl]thio}acetic acid (PTA) and pyridine (PY) have been calculated with Gaussian 94 and Hybrid B3LYP functional density with 6-31G* basis set. Moreover, the electronic properties such as highest occupied molecular orbital (HOMO), lowest unoccupied orbital (LUMO) energy and molecular densities have been investigated.

1. Introduction

The chemistry of heterocyclic molecules containing functional group and heteroelement atoms is attracting current interest in life sciences due to their specificity for biological targets (Franzén, 2000; Masayoshi et al., 1989). These compounds are also of importance for building polynuclear complexes (Bianchini et al., 1999) as models for bioorganic systems (Sorrell et al., 1991; Bouwman et al., 1985; Chen et al., 1991; Pate et al., 1987; Nelson et al., 1983) as well as for the discovery of new catalyst precursors (Togni and Venanzi, 1994). A number of these compounds were found to be excellent inhibitors of copper corrosion (Dafali et al., 2002; Touzani et al., 2001). The presence of nitrogen, oxygen, phosphorous and sulphur in these molecules has a major effect on the inhibition efficiency and consequently on the phenomenon of adsorption on some metals surface. In this article, we design five molecules

* Corresponding author at: Laboratoire de Chimie Appliquée et Environnement, Département de Chimie (URAC 18), Faculté des Sciences, Mohammed 1er, BP: 717, 60 000 Oujda, Morocco. Tel.: +212 677 968 240.
** Corresponding author.
E-mail addresses: touzanir@yahoo.fr (R. Touzani), hammoutib@gmail.com (B. Hammouti).

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based on heterocyclic functional pyridine and pyrimidine such as 1-{2-[(2-hydroxyethyl)thio]ethyl}pyrrolidin-2-one (HTEP) (Bouklah et al., 2006; Tsuji et al., 1989; Lindstrom et al., 1984); [2-(2-oxo-pyrrolidin-1-yl)-ethyl]-phosphonic acid diethyl ester (EOEP) (Prishchenko et al., 2006; Hendricks and Walz, 1976); {[2-(2-oxopyrrolidin-1-yl)ethyl]thio}acetic acid (OETA) (Bouklah et al., 2006); (2-pyridin-4-yl-ethyl]thio}acetic acid (PTA) (Scheefers and Scheefers-Borchel, 2008; Bouklah et al., 2005); pyridine (PY) (Batchelor et al., 2010) (Fig. 1). Theoretical calculations were carried out with Gaussian 94 (Frisch et al., 1995). A conformation analysis was performed, for the inhibitors, on all bonds using an option "scan" in the EMO program, and then founded structures were minimized using Molecular Force Field EMO (MM2-Allinger) and fully optimized at DFT level using Hybrid B3LYP functional density with 6-31G* basis set.

2. Calculations methods

Quantum mechanical geometry optimizations, thermodynamic properties, dipole moments and frontier molecular orbital properties of all compounds were performed with the Gaussian 94 program package (Frisch et al., 1995). They were carried out by using the 6-31G* basis set. Calorific capacities, heats of formation and entropies have been calculated at different temperatures: 100, 298.15, 1000, 1200, 1500 and 2000 K. In order to understand the phenomenon of corrosion, we examined the molecular HOMOs (presumably the π_{donor}) and molecular LUMOs (presumably the $\pi_{acceptor}$) generated via Gaussian 94 by using the HF/6-31G* method (Table 1).

The 1-{2-[(2-hydroxyethyl)thio]ethyl}pyrrolidin-2-one (HTEP) and {[2-(2-oxopyrrolidin-1-yl)ethyl]thio}acetic acid (OETA) were synthesized and tested as corrosion inhibitors for steel in 0.5 M H_2SO_4. The study was carried out by weight loss measurements, potentiodynamic polarization, linear polarization resistance (Rp) and electrochemical impedance spectroscopy (EIS) methods. The inhibition efficiency increases with the concentration of HTEP to attain 89% at 5×10^{-3} M with good agreement between the various methods explored. Therefore, theoretical studies will be a good set to explain these results.

3. Results and discussion

The corrosion inhibition of steel and copper or their alloys by different heterocyclic compounds such as pyrazol, triazole, imidazole and tetrazole derivatives depends essentially on the structure of the inhibitor itself which includes the number of adsorption active centre in the molecule, the nature of the metal and the aggressive solution (Attayibat et al., 2009; Zucchi et al., 1996). To investigate the influence of electronic structure on the efficiency of synthesis of bipyrazolic compounds: 1-{2-[(2-hydroxyethyl)thio]ethyl}pyrrolidin-2-one (HTEP); [2-(2-oxo-pyrrolidin-1-yl)-ethyl]-phosphonic acid diethyl ester (EOEP); {[2-(2-oxopyrrolidin-1-yl)ethyl]thio}acetic acid (OETA); (2-pyridin-4-yl-ethyl]thio}acetic acid (PTA); pyridine (PY), some parameters such as the energy of molecular orbital, E_{HOMO}, E_{LUMO} and the dipole moment (μ) were carried out. The results are given in Table 1. The energy of HOMO is often associated with the electron-donating ability of a molecule; high values of E_{HOMO} are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy and empty molecular orbital. Therefore, the energy of LUMO indicates the ability of the molecule to accept electrons (Larabi et al., 2005; Lukovits et al., 1998). The presence of five atoms of nitrogen in the molecules has a major effect on the inhibition efficiencies and consequently on the phenomenon of adsorption on the copper surface. These five atoms of nitrogen constitute an active adsorption

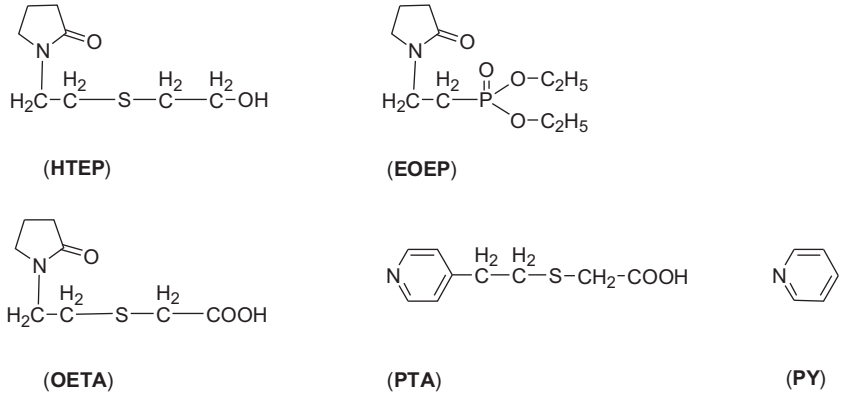

Figure 1 Molecular structure of the inhibitors.

Table 1 Eelctronic properties for the inhibitors.

	E. Totale u.a.	E(HOMO) u.a.	E(LUMO) u.a.	ΔE u.a.	μ Debye	E%
EOEP	−1090.2006	−0.2428	0.0229	0.2657	3.7437	86
PTA	−952.9752	−0.2366	−0.0245	0.2122	4.4754	82
HTEP	−917.2736	−0.2239	0.0244	0.2483	5.2577	89
OETA	−991.3242	−0.2324	−0.0058	0.2266	4.1691	83
PY	−248.2850	−0.2526	−0.0225	0.2301	2.1921	17

centre in these inhibitors. Following the E_{HOMO} from Table 1 looks apparently easier for the molecule to offer electrons to unoccupied d-orbitals of copper and in that case the higher inhibition efficiency is expected. The higher HOMO energy from HTEP ⁄ OETA ⁄ EOEP and PTA ⁄ PY can be used as one of the parameters for the explanation of its good inhibitors performance. Consequently, the smaller energy gap is reflected in a stronger chemisorptions bond and perhaps greater inhibition efficiency (Finley and Hackerman, 1960). Lower values of dipole moments (μ) will favour accumulation of the inhibitor in the surface layer and therefore higher inhibition efficiency (Khalil, 2003). Meanwhile, several authors state that the inhibition efficiency increases with increasing values of dipole moment (Lagrenée et al., 2001; Quraishi and Sardar, 2003). On the other hand, survey of the literature reveals that several irregularities appeared in case of correlation of dipole moment with inhibitor of efficiency (Khaled et al., 2005; Bereket et al., 2002) (Figs. 2 and 3).

4. Conclusion

It can be concluded on the basis of the result obtained that the:

- The selection of parameters is in important step in theoretical study. The relationship between the parameter(s) and activity should be strong, and therefore efficiency predictions will be more promising.

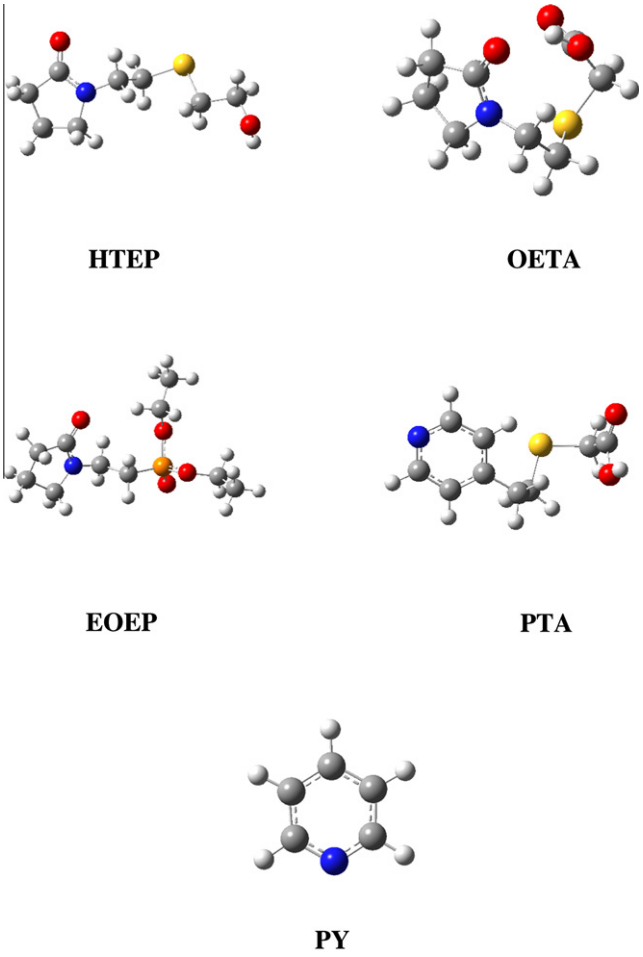

Figure 2 Optimized structures of the studied inhibitors.

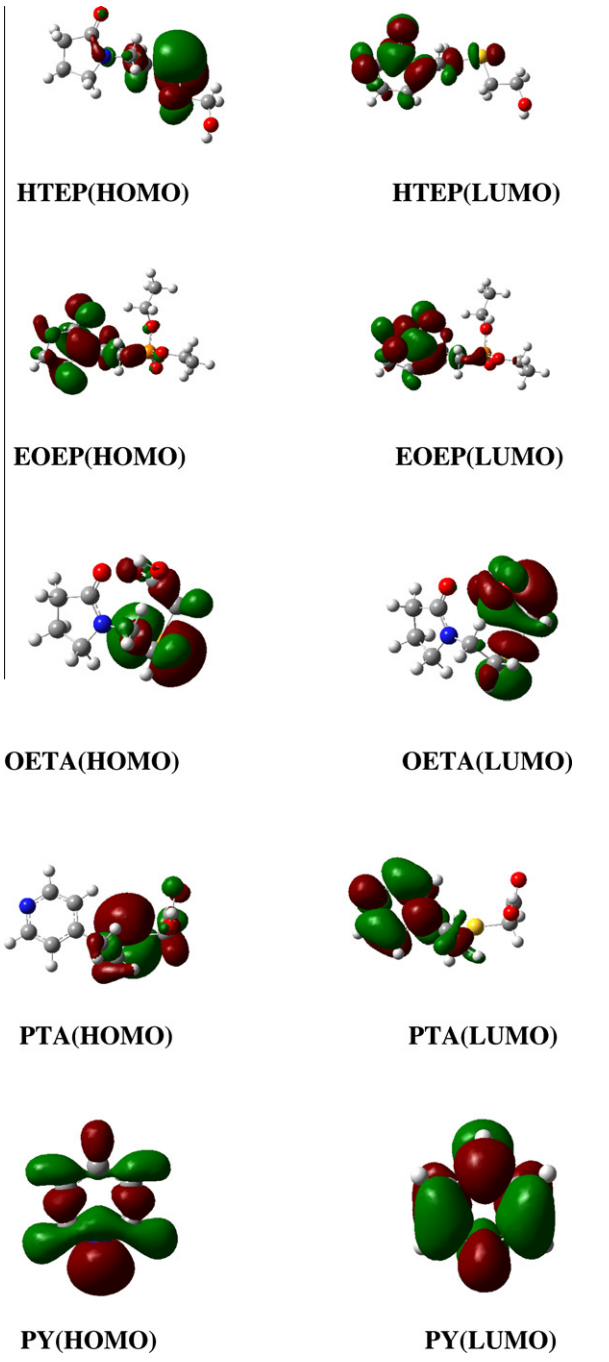

Figure 3 Orbital form for all these compounds.

- The high values of the thermodynamic parameters suggest higher stability for molecules studied.
- The HOMO energy calculations show that bipy1 molecule has the higher energy therefore they could be better corrosion inhibitors of the series studied.
- The estimation *a priori* of the parameters discussed by quantum-chemical methods is important for the molecular design of compounds with given properties and may serve as the basis for the acceptance of expert solutions on the expediency of a synthesis, laborious, prolonged, requiring complex apparatus, vigorous conditions, with expensive and toxic reagents.

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