

Theoretical approach to the corrosion inhibition efficiency of some quinoxaline derivatives of steel in acid media using the DFT method

A. Zarrouk · I. El Ouali · M. Bouachrine ·
B. Hammouti · Y. Ramli · E. M. Essassi · I. Warad ·
A. Aouniti · R. Salghi

Received: 4 May 2012 / Accepted: 29 May 2012
© Springer Science+Business Media B.V. 2012

Abstract Corrosion inhibition efficiencies of 1,4-dihydroquinoxaline-2,3-dione (Q1) and 2-phenylthieno[2,3-*b*]quinoxaline (Q2) as corrosion inhibitors against the corrosion of steel surface in hydrochloric acid is studied by means of density functional approach B3LYP/6-31G calculations. Quantum chemical parameters such as highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), the fraction of electrons transferred (ΔN), the global electrophilicity ω ,

A. Zarrouk (✉) · I. El Ouali · B. Hammouti · A. Aouniti
LCAE-URAC18, Faculté des Sciences, Université Mohammed 1er, Oujda, Morocco
e-mail: azarrouk@gmail.com

M. Bouachrine
UMIM, Faculté Polydisciplinaire de Taza, Université Sidi Mohamed Ben Abdellah, Taza, Morocco

Y. Ramli · E. M. Essassi
Laboratoire de Chimie Organique Hétérocyclique, URAC 21, Université Mohammed V-Agdal, Rabat, Morocco

Y. Ramli
Laboratoire Nationale de Contrôle des Médicaments, BP 6206, Rabat, Morocco

Y. Ramli · E. M. Essassi
Morocco et Institute of Nanomaterials and Nanotechnology, MAScIR, Rabat, Morocco

I. Warad
Department of Chemistry–College of Science, King Saud University, B.O. 2455, Riyadh 11451, Saudi Arabia

R. Salghi
Equipe de Génie de l'Environnement et Biotechnologie, ENSA, Université Ibn Zohr, BP 1136, Agadir, Morocco

and the total energy were calculated. All calculations have been performed by considering density functional theory using the GAUSSIAN03W suite of programs.

Keywords Steel · Hydrochloric acid · Quinoxalines · Corrosion · DFT method

Introduction

The study of corrosion inhibition is a very active field of research. Several classes of organic compounds are widely used as corrosion inhibitors for metals in acid environments [1–8]. Experimental means are useful to explain the inhibition mechanism but they are often expensive and time-consuming. Ongoing hardware and software advances have opened the door for the powerful use of theoretical chemistry in corrosion inhibition research. Several quantum chemical methods and molecular modeling techniques have been performed to correlate the inhibition efficiency of the inhibitors with their molecular properties [9–15]. Using theoretical parameters helps to characterize the molecular structure of the inhibitors and to propose their interacting mechanism with surfaces [16]. Some studies have shown that the inhibition of the corrosion process is mainly described by the formation of donor–acceptor surface complexes between free or π -electrons of an organic inhibitor, mostly containing nitrogen, sulfur or oxygen atoms, and a vacant d-orbital of a metal [17–26]. Among the various nitrogenous compounds studied as inhibitors, quinoxalines have been considered as environmentally acceptable chemicals. Many substituted quinoxaline compounds have been recently studied in considerable detail as effective corrosion inhibitors for steel and copper in acidic media [27–35].

The inhibitive properties of five different organic compounds, 1,4-dihydroquinoxaline-2,3-dione (Q1), and 2-phenylthieno[2,3-*b*]quinoxaline (Q2) have been reported in a previous experimental study [30, 36]. The aim of this paper is to extend these investigations in order to discuss the relationship between quantum chemical calculations and experimental inhibition efficiencies of the inhibitors by determining the quantum chemical parameters such as the energies of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO} , dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), the fraction of electrons transferred (ΔN), and the total energy (TE). The chemical structures of the compounds studied are given in Fig. 1.

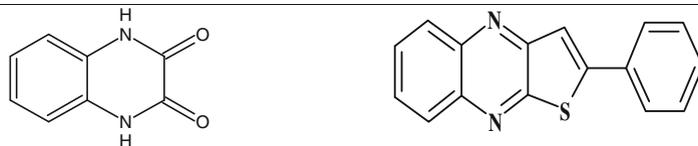


Fig. 1 The molecular structures of the investigated inhibitors: 1,4-dihydroquinoxaline-2,3-dione (Q1) and 2-phenylthieno[2,3-*b*]quinoxaline (Q2)

Computational details

Density functional theory (DFT) methods were used in this study. These methods have become very popular in recent years because they can reach exactitude similar to other methods (ab initio, QSAR: quantitative structure–activity relationships, etc.) in less time, and they are less expensive from the computational point of view. In agreement with the DFT results, the energy of the fundamental state of a polyelectronic system can be expressed through the total electronic density, and, in fact, the use of electronic density instead of wave function for calculating the energy constitutes the fundamental base of DFT [37]. All calculations were done by GAUSSIAN03W software [38], using the B3LYP functional [39, 40] and a 6-31G* basis set [40]. The B3LYP, a version of the DFT method, uses Becke's three-parameter functional (B3) and includes a mixture of HF with DFT exchange terms associated with the gradient corrected correlation functional of Lee, Yang, and Parr (LYP) [39, 40]. The geometry of all species under investigation was determined by optimizing all geometrical variables without any symmetry constraints. Frontier molecular orbitals (HOMO and LUMO) may be used to predict the adsorption centers of the inhibitor molecule. For the simplest transfer of electrons, adsorption should occur at the part of the molecule where the softness, σ , which is a local property, has the highest value. According to Koopman's theorem [41], the energies of the HOMO and the LUMO orbitals of the inhibitor molecule are related to the ionization potential, I , and the electron affinity, A , respectively, by the following relationships: $I = -E_{\text{HOMO}}$ and $A = -E_{\text{LUMO}}$. Absolute electronegativity, χ , and absolute hardness, η , of the inhibitor molecule are given by [42]. $\chi = \frac{I+A}{2}$ and $\eta = \frac{I-A}{2}$. The softness is the inverse of the hardness: $\sigma = \frac{1}{\eta}$.

Electronegativity, hardness, and softness have proved to be very useful quantities in chemical reactivity theory. When two systems, Fe and inhibitor, are brought together, electrons will flow from lower χ (inhibitor) to higher χ (Fe), until the chemical potentials become equal. The number of transferred electrons (ΔN) was also calculated [43] by using the equation below: $\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{inh}}}{2(\eta_{\text{Fe}} + \eta_{\text{inh}})}$

Where χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and inhibitor molecule, respectively η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule, respectively.

In this study, we use the theoretical value of $\chi_{\text{Fe}} = 7 \text{ eV/mol}$ and $\eta_{\text{Fe}} = 0 \text{ eV/mol}$ for the computation of number of transferred electrons [41]. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance [44]. The global electrophilicity index was introduced by Parr [45] and is given by $\omega = \frac{\mu^2}{2\eta}$. According to the definition, this index measures the propensity of chemical species to accept electrons. A good, more reactive, nucleophile is characterized by lower value of μ , ω ; and conversely a good electrophile is characterized by a higher value of μ , ω . This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment.

Results and discussion

The inhibition of steel using substituted quinoxalines as corrosion inhibitors were investigated experimentally. Table 1 indicates clearly a decrease in the corrosion rate in the presence of Q1 and Q2. This effect is greatly marked at higher concentrations of inhibitors. The inhibitive action is more explicit by $E_w\%$ data which increases with inhibitor concentration to reach 95 % for Q1 and 87 % for Q2.

Quantum chemical methods have already proven to be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity [46]. Thus, it has become a common practice to carry out quantum chemical calculations in corrosion inhibition studies. The predicted properties of reasonable accuracy can be obtained from DFT calculations [47, 48]. All quantum chemical properties were obtained after geometric optimization with respect to all the nuclear coordinates using the Kohn–Sham approach at the DFT level. The optimized molecular structures of the studied molecules using hybrid DFT functional [B3LYP/6-31G* (d)] are shown in Fig. 2.

The computed quantum chemical properties such as energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), HOMO–LUMO energy gap ($\Delta E_{\text{H-L}}$), dipole moment (μ) and total energy (TE), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), the global electrophilicity (ω), the fraction of electrons transferred from the inhibitor to iron surface (ΔN), and the total energy (TE) are given in Table 2.

Table 1 Corrosion rate of steel in 1 M HCl with and without quinoxaline derivatives at various concentrations, and the corresponding inhibition efficiency at 6 h [30, 36]

Conc (M)	Q1 E_w (%)	Q2 E_w (%)
Blank	–	–
1×10^{-6}	17	32
5×10^{-6}	29	43
1×10^{-5}	43	69
5×10^{-5}	61	86
1×10^{-4}	70	93
5×10^{-4}	87	95

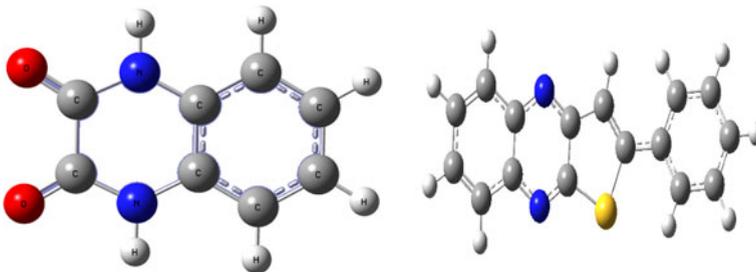


Fig. 2 Optimized structure of studied molecules obtained by B3LYP/6-31G* level

Table 2 Calculated quantum chemical parameters of the studied compounds

Quantum parameters	Q1	Q2
E_{HOMO} (eV)	-6.1367	-5.9449
E_{LUMO} (eV)	-1.4046	-2.2214
ΔE gap (eV)	4.7321	3.723
E_w %	87	95
μ (debye)	6.2718	1.4513
$I = -E_{\text{HOMO}}$ (eV)	6.1367	5.9449
$A = -E_{\text{LUMO}}$ (eV)	1.4046	2.2214
$\chi = \frac{I+A}{2}$ (eV)	3.77065	4.08315
$\eta = \frac{I-A}{2}$ (eV)	2.36605	1.86175
$\sigma = \frac{1}{\eta}$	0.422645337	0.53712904
$\omega = \frac{\mu^2}{2\eta}$	8.31248	0.56567
$\Delta N = \frac{\chi_{\text{Fc}} - \chi_{\text{inh}}}{2(\eta_{\text{Fc}} + \eta_{\text{inh}})}$	15.28161	10.8609
TE (eV)	-15,461.7176	-30,557.3333

The inhibition effect of inhibitor compound is usually ascribed to adsorption of the molecule on the metal surface. There can be physical adsorption (physisorption) and chemical adsorption (chemisorption) depending on the adsorption strength. When chemisorption takes place, one of the reacting species acts as an electron pair donor and the other one acts as an electron pair acceptor. The energy of the highest occupied molecular orbital (E_{HOMO}) measures the tendency towards the donation of electron by a molecule [49]. High values of E_{HOMO} have a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy, empty molecular orbital. Increasing values of E_{HOMO} facilitate adsorption and therefore enhance the inhibition efficiency, by influencing the transport process through the adsorbed layer. Therefore, higher values of E_{HOMO} indicate better tendency towards the donation of electron, enhancing the adsorption of the inhibitor on mild steel and therefore better inhibition efficiency. E_{LUMO} indicates the ability of the molecule to accept electrons.

The binding ability of the inhibitor to the metal surface increases with increasing of the HOMO and decreasing of the LUMO energy values.

In Fig. 3, we have presented the frontier molecule orbital density distributions of the studied compound: HOMO (right), LUMO (left). Analysis of this figure shows that the distribution of two energies HOMO and LUMO for Q1 and Q2 are localized in the atoms of the aromatic cycles and on the substituents of the two compounds.

According to the frontier molecular orbital theory (FMO) of chemical reactivity, the transition of electrons is due to interaction between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of reacting species [50]. E_{HOMO} is a quantum chemical parameter which is often associated with the electron donating ability of the molecule. A high value of E_{HOMO} is likely a tendency of the molecule to donate electrons to appropriate the acceptor molecule of low empty molecular orbital energy [51]. The inhibitor does not only donate electrons to the unoccupied d orbital of the metal ion but can also

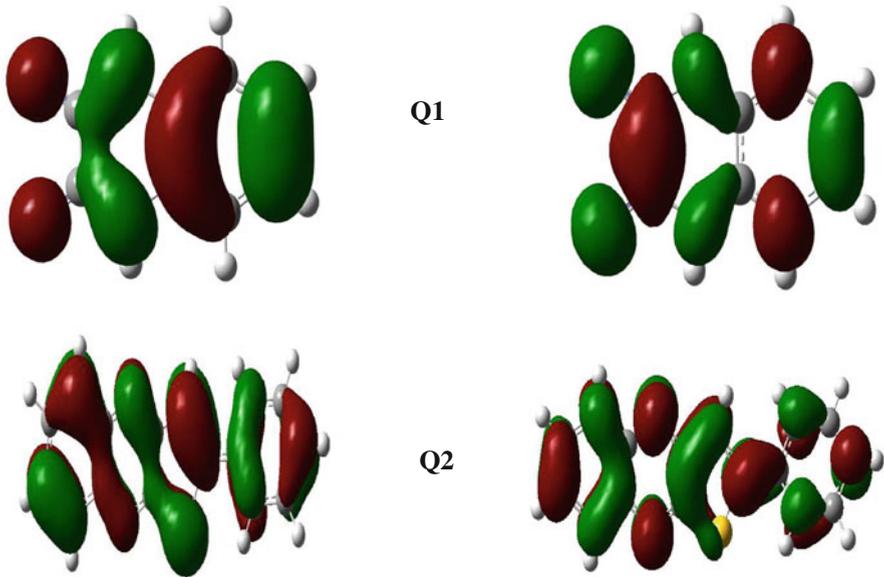


Fig. 3 Schematic representation of HOMO and LUMO molecular orbital of the studied molecules, Q1 and Q2

accept electrons from the d-orbital of the metal leading to the formation of a feedback bond. The highest value of $E_{\text{HOMO}} - 5.9449$ (eV) of Q2 indicates a better inhibition efficiency.

It has also been found that an inhibitor does not only donate an electron to the unoccupied d-orbital of the metal ion but can also accept electrons from the d-orbital of the metal leading to the formation of a feedback bond. Therefore, the tendency for the formation of a feedback bond would depend on the value of E_{LUMO} . The lower the E_{LUMO} , the easier is the acceptance of electrons from the d-orbital of the metal [52]. Based on the values of E_{LUMO} , the order obtained for the decrease in inhibition efficiency ($Q2 > Q1$) was also similar to the one obtained from the experimental results.

The separation energy, $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$, is an important parameter as a function of reactivity of the inhibitor molecule towards the adsorption on the metallic surface. As ΔE decreases, the reactivity of the molecule increases, leading to an increase in the inhibition efficiency of the molecule. The results obtained from quantum chemical calculations are listed in Table 2.

The calculations indicate that Q2 has the lowest value, which means the highest reactivity, among the other inhibitors and, accordingly, the highest inhibition efficiency which agrees well with the experimental observations. The order of reactivity in this case will be: $Q2 > Q1$

Absolute hardness and softness are important properties for measuring the molecular stability and reactivity. It is apparent that the chemical hardness

fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions, or molecules under small perturbations of the chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap [53]. In our present study, Q2 with a low hardness value of 1.86175 (eV) was compared with other compounds having a low energy gap.

Normally, the inhibitor with the least value of global hardness (hence the highest value of global softness) is expected to have the highest inhibition efficiency [54]. For the simplest transfer of electrons, adsorption could occur at the part of the molecule where softness (σ), which is a local property, has a highest value [55]. Q2 with the softness value of 0.53712904 has the highest inhibition efficiency.

The total energy of the best inhibitor Q2 is equal to $-30,557.3333$ eV. This result indicated that the Alizarin molecule is favorably adsorbed through the active centers of adsorption.

The dipole moment (μ in Debye) is another important electronic parameter that results from non-uniform distribution of charges on the various atoms in the molecule [56]. The high value of dipole moment probably increases the adsorption between the chemical compound and the metal surface [57]. The energy of the deformability increases with the increase in μ , making the molecule easier to adsorb at the Fe surface. The volume of the inhibitor molecules also increases with the increase of μ . This increases the contact area between the molecule and the surface of iron and increases the corrosion inhibition ability of inhibitors. In our study, there is no direct relationship between the IE and the dipole moment.

In the literature, it has been reported that the values of ΔN show an inhibition effect resulting from electrons donation [58, 59]. According to Lukovits's study [59], if the value of ΔN was greater than 3.6, the inhibition efficiency increased with the increasing electron donating ability of the inhibitor at the metal surface. Also, it was observed [60] that inhibition efficiency increased with an increase in the values of ΔN . However, our study reveals that there is no regular trend in the inhibition efficiency by increasing values of ΔN .

Conclusion

Using the DFT/B3LYP method, the inhibition efficiency of some substituted quinoxalines is investigated leading to the following conclusions:

- Through DFT calculations, a correlation between parameters related to the electronic and molecular structures of some quinoxaline derivatives and their ability to inhibit the corrosion process could be established.
- The inhibition efficiency of quinoxaline derivatives obtained quantum chemically increase with the increase in E_{HOMO} , and decrease in E_{LUMO} and energy gap (ΔE). Q2 has the highest inhibition efficiency because it had the highest HOMO energy.
- The parameters like hardness (η) and softness (σ) confirms the inhibition efficiency in the order of $Q2 > Q1$.

- The total energy of the best inhibitor, Q2, is the lowest among the compounds studied. This result indicated that Q2 is favorably adsorbed through the active centers of adsorption on the steel surface.
- In our study, there is no direct relationship between the inhibition efficiency and the dipole moment (μ) and the number of transferred electrons (ΔN)

References

1. M.A. Shaker, H.H. Abdel-Rahman, *Am. J. Appl. Sci.* **4**, 554 (2007)
2. S. Xia, M. Qiu, L. Yu, F. Liu, H. Zhao, *Corros. Sci.* **50**, 2021 (2008)
3. M.S. Abdel-Aal, M.S. Morad, *Br. Corros. J.* **36**, 253 (2001)
4. M.M. El-Naggar, *Corros. Sci.* **49**, 2226 (2007)
5. Y. Feng, K.S. Siow, W.K. Teo, A.K. Hsieh, *Corros. Sci.* **41**, 829 (1999)
6. H.L. Wang, R.B. Liu, J. Xin, *Corros. Sci.* **46**, 2455 (2004)
7. G. Mu, X. Li, *J. Coll. Interf. Sci.* **289**, 184 (2005)
8. L. Larabi, Y. Harek, O. Benali, S. Ghalem, *Prog. Org. Coat.* **54**, 256 (2005)
9. G. Gece, *Corros. Sci.* **50**, 2981 (2008)
10. H.J. Henriquez-Roman, L. Padilla-Campos, M.A. Paez, J.H. Zagal, M.A. Rubio, C.M. Rangel, J. Costamagna, G. Cardenas-Jiron, *J. Mol. Struct. (THEOCHEM)* **757**, 1 (2005)
11. N. Khalil, *Electrochim. Acta* **48**, 2635 (2003)
12. M. Behpour, S.M. Ghoreishi, N. Soltani, M. Salavati-Niasari, M. Hamadani, A. Gandomi, *Corros. Sci.* **50**, 2172 (2008)
13. M.K. Awad, R.M. Issa, F.M. Atlam, *Mater. Corros.* **60**, 813 (2009)
14. M.K. Awad, *J. Electroanal. Chem.* **567**, 219 (2004)
15. I.N. Levine, *Quantum Chemistry* (Prentice Hall, New Jersey, 1991)
16. M.A. Quraishi, R. Sardar, D. Jamal, *Mater. Chem. Phys.* **71**, 309 (2001)
17. R.M. Issa, M.K. Awad, F.M. Atlam, *Mat. Corros.* **61**, 709 (2010)
18. M.A. Amina, Q. Mohsenb, O.A. Hazzazic, *Mater. Chem. Phys.* **114**, 908 (2009)
19. M. Scendo, *Corros. Sci.* **49**, 2985 (2007)
20. R.M. Issa, M.K. Awad, F.M. Atlam, *Appl. Surf. Sci.* **255**, 2433 (2008)
21. M.S. Sahin, G. Gece, F. Karci, S. Bilgic, *J. Appl. Electrochem.* **38**, 809 (2008)
22. M.K. Awad, F.M. Mahgoub, M.M. El-iskandrani, *J. Mol. Struct. (THEOCHEM)* **531**, 105 (2000)
23. M. Lashkari, M.R. Arshadi, *Chem. Phys.* **299**, 131 (2004)
24. E. Jamalizadeh, S.M.A. Hosseini, A.H. Jafari, *Corros. Sci.* **51**, 1428 (2009)
25. S. Bilgic, N. Caliskan, *J. Appl. Electrochem.* **31**, 79 (2001)
26. G. Gece, S. Bilgic, *Corros. Sci.* **51**, 1876 (2009)
27. M. Benabdellah, R. Touzani, A. Aouniti, A. Dafali, S. Elkadiri, B. Hammouti, M. Benkaddour, *Phys. Chem. News* **37**, 63 (2007)
28. M. Benabdellah, K. Tebbji, B. Hammouti, R. Touzani, A. Aouniti, A. Dafali, S. El Kadiri, *Phys. Chem. News* **43**, 115 (2008)
29. A. Zarrouk, A. Dafali, B. Hammouti, H. Zarrok, S. Boukhris, M. Zertoubi, *Int. J. Electrochem. Sci.* **5**, 46 (2010)
30. I. El Ouali, B. Hammouti, A. Aouniti, Y. Ramli, M. Azougagh, E.M. Essassi, M. Bouachrine, *J. Mater. Environ. Sci.* **1**, 1 (2010)
31. I.B. Obot, N.O. Obi-Egbedi, N.W. Odozi, *Corros. Sci.* **52**, 923 (2010)
32. I.B. Obot, N.O. Obi-Egbedi, *Mater. Chem. Phys.* **122**, 325 (2010)
33. I.B. Obot, N.O. Obi-Egbedi, *Corros. Sci.* **52**, 282 (2010)
34. B. Hammouti, A. Zarrouk, S.S. AL-Deyab, I. Warad Oriental, *J. Chem.* **27**, 23 (2011)
35. M. Elayyachy, B. Hammouti, A. El Idrissi, A. Aouniti, *Port. Electrochim. Acta* **29**, 57 (2011)
36. I. El Ouali, B. Hammouti, A. Aouniti, M. Benabdellah, S. Kertit, *Der. Pharm. Chem.* **3**, 294 (2011)
37. C. Öğretir, G. Berekci, *J. Mol. Struct. (THEOCHEM)* **488**, 223 (1999)
38. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B.

- Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi 870 H. Ju et al./Corros. Sci. **50**, 865–871 (2008)
39. C.Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.02, (Gaussian, Pittsburgh, 2003)
 40. S.G. Zhang, W. Lei, M.Z. Xia, F.Y. Wang, J. Mol. Struct. (THEOCHEM) **732**, 175 (2005)
 41. V.S. Sastri, J.R. Perumareddi, Corrosion **53**, 671 (1996)
 42. R.G. Pearson, Inorg. Chem. **27**, 734 (1988)
 43. S. Martinez, Mater. Chem. Phys. **77**, 97 (2002)
 44. A. Rauk, *Orbital Interaction Theory of Organic Chemistry*, 2nd edn. (Wiley, New York, 2001), p. 34
 45. H. Chermette, J. Comput. Chem. **20**, 129 (1999)
 46. R.G. Parr, L. Szentpaly, S. Liu, J. Am. Chem. Soc. **121**, 1922 (1999)
 47. E. Kraka, D. Cremer, J. Am. Chem. Soc. **122**, 8245 (2000)
 48. C. Adamo, V. Barone, Chem. Phys. Lett. **330**, 152 (2000)
 49. M. Parac, S. Grimme, J. Phys. Chem. A **106**, 6844 (2003)
 50. A.Y. Musa, A.H. Kadhum, A.B. Mohamad, A.B. Rohoma, H. Mesmari, J. Mol. Struct. **969**, 233 (2010)
 51. G. Gece, S. Bilgic, Corros. Sci. **51** 1876 (2009)
 52. H. Wang, X. Wang, H. Wang, L. Wang, A. liu, J. Mol. Model. **13**, 147 (2007)
 53. N.O. Obi-Egbedi, I.B. Obot, M.I. El-Khaiary, S.A. Umoren, E.E. Ebenso, Int. J. Electrochem. Sci. **6**, 5649 (2011)
 54. E.E. Ebenso, D.A. Isabirye, N.O. Eddy, Int. J. Mol. Sci. **11**, 2473 (2010)
 55. R. Hasanov, M. Sadikoglu, S. Bilgic, Appl. Surf. Sci. **253**, 3913 (2007)
 56. O. Kikuchi, Quant. Struct.-Act. Relat. **6**, 179 (1987)
 57. X. Li, S. Deng, H. Fu, T. Li, Electrochim. Acta. **54**, 4089 (2009)
 58. V.S. Sastri, J.R. Perumareddi, Corrosion. **53**, 671 (1997)
 59. I. Lukovits, E. Kalman, F. Zucchi, Corrosion. **57**, 3 (2001)
 60. H. Ju, Z.P. Kai, Y. Li, Corros. Sci. **50**, 865 (2008)