
Reactivity Properties of Derivatives of 2-Imidazoline: An ab initio DFT Study

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ABSTRACT: The structural and electronic properties of a series of imidazoline (I) derivatives R1-I-R2 have been studied by means of density functional theory. The chosen compounds have different chain lengths (R1) and pendant (R2) groups, where R1 = —CH₃, —(CH₂)_n—CH₃ (*n* = 2, 4, . . . , 16) and R2 = H, CH₃, C₂H₅, C₃H₇, C₂H₅—OH, C₂H₅—NH₂, C₂H₅—SH, C₂H₅—COOH, and C₂H₅—Cl. All-electron calculations were carried out by means of the Gaussian-98 program. Natural and Mulliken population analysis were determined for each of the neutral and charged molecules. The reactivity was analyzed in terms of the Fukui indices. The results indicate a high reactivity for both the tertiary (showing the biggest) and the iminic nitrogen atoms of the imidazoline ring. Although the N site of the pending groups has a much lower reactivity, this is significantly increased when a sulfur atom replaces it. In general, the reactivity of the N atoms of the ring depends significantly on the substituents. As expected, the frontier molecular orbitals, highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO), also describe the reactivity behavior. As the size of the R1 chain increases, the two N atoms of the ring increase their nucleophilic character, since the HOMOs become more highly located. The obtained results help to explain the observed increased activity of these derivatives when they are used as inhibitors of corrosion moieties on metallic surfaces.

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Finally, the solvent effects on the ground-state geometry were studied for one of the most promising reactive imidazolines; for which its interaction with an iron oxide surface was also addressed. © 2001 John Wiley & Sons, Inc. Int J Quantum Chem 85: 546–556, 2001

Key words: corrosion inhibitors; DFT calculations; Fukui indices; reactivity

Introduction

Imidazoline derivatives are an extensive group of compounds that behave as cationic surfactants [1], depending on the nature of hydrocarbon or substituents groups attached to the carbon or nitrogen atoms of the imidazoline ring. They are used as water repellents, anticorrosives, emulsifiers and dispersing agents, adhesion promoters, and textile softeners [1]. These heterocyclic derivatives are usually synthesized by the condensation reaction of ethylenediamines with carboxylic acids [1]. The 1,3-diazacyclopentene ring is partially hydrolyzed in hot water and almost completely hydrolyzed when it is treated with diluted acids [2]. It should be noted that the imidazoline ring cannot be obtained by direct hydrogenation of the corresponding imidazole parent because imidazoles are just reduced to yield amines and/or aldehydes [3].

From the technological side, imidazolines have important applications for reducing corrosion. For example, the corrosion of pipes in the petrochemical industry is a severe problem causing losses of millions of dollars per year. As a result, the study of the corrosion processes is a very active field of research [4] and represents a strong motivation for the present study. In this regard, imidazoline derivatives represent a promising alternative for the design of "green" corrosion inhibitors that, due to its biodegradability, will satisfy the environmental requirements that are currently imposed on the development of cleaner chemical inhibitors [5]. Some corrosion inhibitors, such as thiourea derivatives, have been studied by semiempirical techniques [6]. However, despite the wide number of applications, to our knowledge, the reactivity of the 1-imidazoline ring has not been studied either experimentally or theoretically.

The main aim of this work is to study the structure, characteristics, and reactivity of these compounds by theoretical methods. Therefore, the features that contribute to making these kinds of compounds good candidates as corrosion inhibitors have been studied in terms of their structural and

electronic properties. In particular, the local reactivity has been studied using the Fukui indices approach [7]; this method will indicate both the location of the reactive regions as well as either the nucleophilic or electrophilic behavior.

Furthermore, an insight of the reactivity of the compounds has been obtained by the analysis of the frontier orbitals as well as on the type of charge distribution present. Finally, we also analyze the effects that the solvent produces on the structural parameters for one of the most promising reactive derivatives. Moreover, to obtain more details of the relationship between the reactivity and the inhibition of corrosion properties, we have studied the interaction of a high reactive derivative with an iron oxide surface.

Since their original proposal, the Fukui functions have proven to be very useful for the characterization of the reactivity behavior of several π -type systems [8]. Furthermore, Fukui functions were defined by Parr and Yang [9] as partial derivatives, under a constant external potential, of the electron density with respect to the number of electrons. In practice, finite-differences can be used to write and evaluate the Fukui indices as linear combinations of the changes in electron density that would be expected to occur either from electron attachment or detachment. Several forms of Fukui functions have been proposed because of the well-known derivative discontinuities related to the integer values of the number of electrons [9, 10].

Among the several proposals for the Fukui functions, the expressions:

$$f^+(\mathbf{r}) = q^+(\mathbf{r}) - q(\mathbf{r})$$

and

$$f^-(\mathbf{r}) = q(\mathbf{r}) - q^-(\mathbf{r})$$

represent a measure of reactivity toward nucleophiles and electrophiles, respectively. In the above equations, $q(\mathbf{r})$, $q^+(\mathbf{r})$, and $q^-(\mathbf{r})$ are the charge of the neutral, cationic, and anionic species, respectively. These charges may be obtained through the application of ab initio molecular orbital (MO) calculations using the computational methodologies of quantum chemistry. Indeed, it has been found that the Fukui

indices, as defined above, are very useful parameters for reactivity studies of several types of organic compounds [11].

Computational Procedure

Ab initio calculations for the series of imidazoline derivatives shown in Figures 1(a)–1(c) were carried out using the Gaussian-98 program [12]. The exchange–correlation was treated using hybrid, B3LYP [13, 14], and pure, BLYP [13, 15], functionals. The 6-31G** and 6-311G** orbital basis sets were employed for all atoms [16, 17]. A full optimization was performed in each case. Initially, geometries were optimized with the 6-31G** basis, then, the structures were reoptimized using the 6-311-G** basis sets. It was found that both the B3LYP and BLYP give very similar structures and energetics. In what follows, our reported results correspond to

the B3LYP/6-311G** configuration, which is known to be a highly accurate and practical method [18]. A vibrational analysis was carried out for each optimized molecule, which provides information about their stability and if they are in a minimum or in a transition state. Moreover, through the subtraction and addition of one electron, cations and anions were calculated with the neutral optimized structures. Calculations of the $N + 1$ and $N - 1$ electron species are needed to perform the finite difference approximation involved in the nucleophilic and electrophilic Fukui functions.

The optimized geometries of the studied imidazoline derivatives are shown in Figures 1(a)–1(c). They are 2-methylimidazoline (A), N-methyl-2-methylimidazoline (B), N-ethyl-2-methylimidazoline (C), N-propyl-2-methylimidazoline (D), N-(2-aminoethyl)-2-methylimidazoline (E), N-(2-hydroxyethyl)-2-methylimidazoline (F), N-(2-thioethyl)-2-methylimidazoline (G), N-(2-clo-

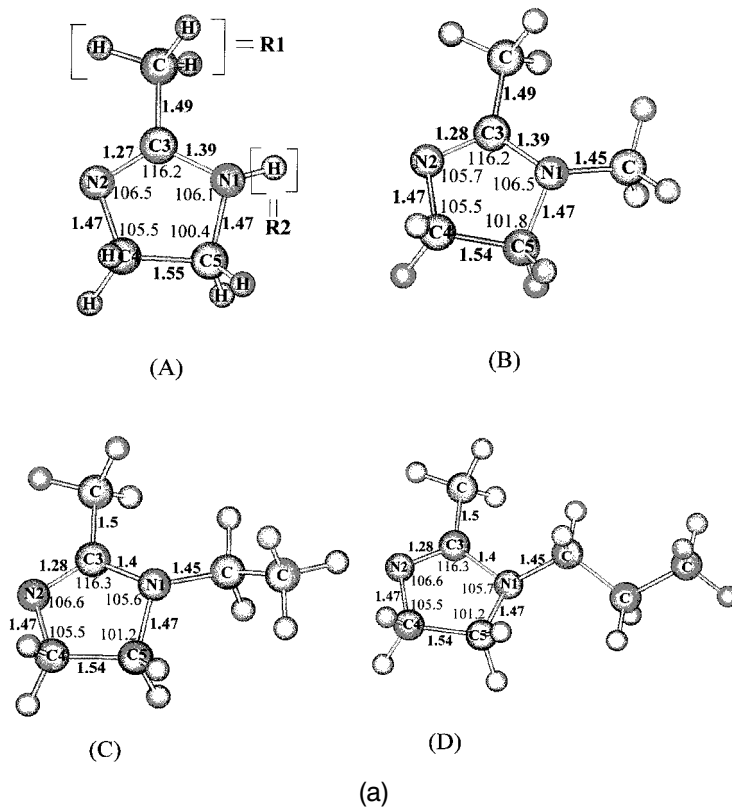


FIGURE 1. (a) Optimized B3LYP/6-311G** structures of the A, B, C, and D imidazoline derivatives. In A, R1 and R2 are labels for the substituents and pendant groups. The bond lengths are in angstroms and bond angles in degrees. (b) Optimized B3LYP/6-311G** structures of the E, F, and G derivatives. The bond lengths are in angstroms and bond angles in degrees. The N--H hydrogen bridge also is indicated. (c) Optimized B3LYP/6-311G** structures of the H and I derivatives. The bond lengths are in angstroms and bond angles in degrees.

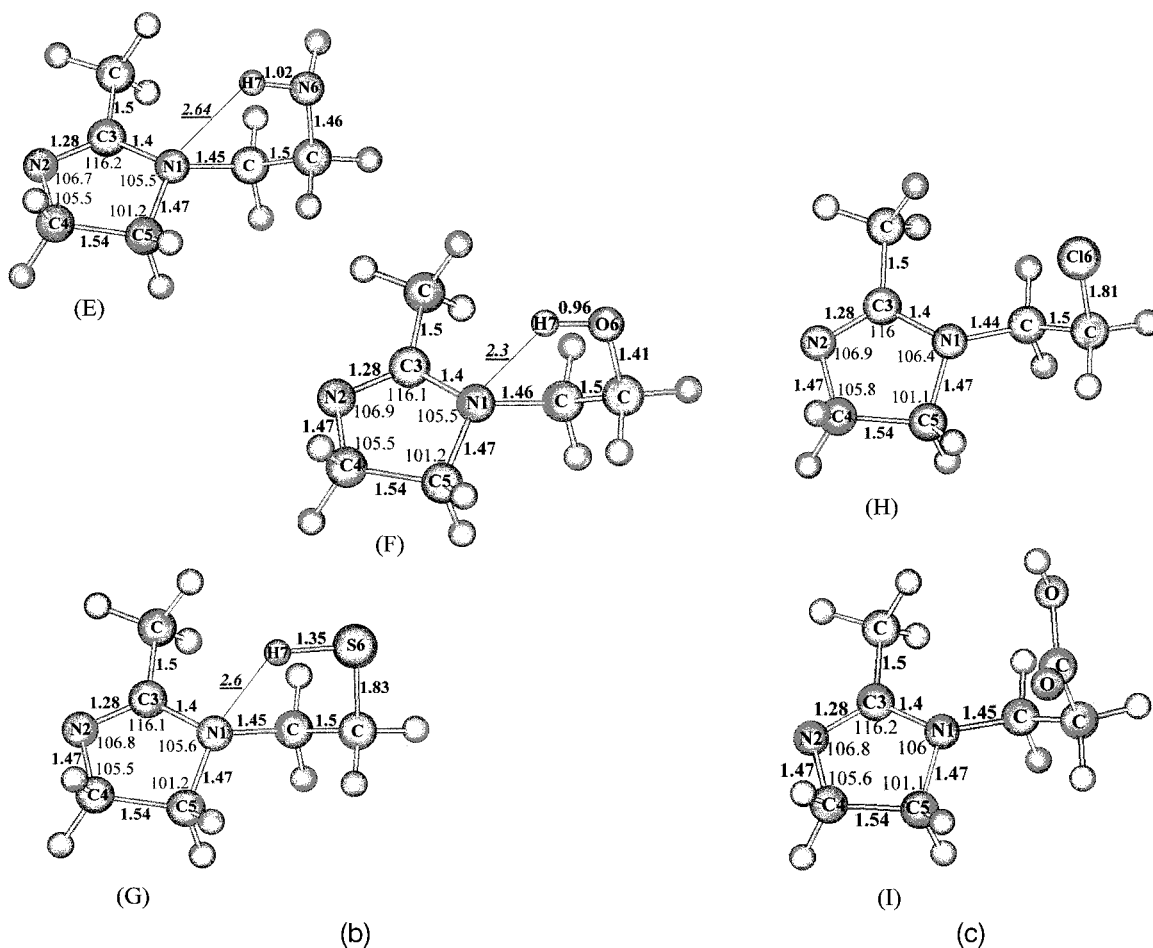


FIGURE 1. (Continued.)

roethyl)-2-methylimidazoline (H), and N-(2-carboxyethyl)-2-methylimidazoline (I). Most of these proposed derivatives have not yet been reported in the literature. So, our results have some predicting character regarding both the geometry and the reactivity properties of these compounds. As mentioned, our goal is to identify the key parameters, structural and/or electronic, of those derivatives that might be used as inhibitors of corrosion. For this purpose, the proposed molecules have been selected since they have the following features: (i) one substituent (R1) methyl group (connected to C2); (ii) a chain (R2), attached to N1, of different size and terminal group. Derivative (E) is included because the hydrocarbonated chain R1, which is bonded to C2, is of greater length, as indicated in Figure 2. Substituent effects are useful in understanding how the replacement of atoms or groups in the derivatives will affect their reactivity patterns. We believe that the selected chemical

substitutions allow a more clear determination of the active sites. Even more, characteristics of the sites provide valuable information concerning the capability for the inhibition of corrosion of a given derivative. In a first approach, anticorrosion involves the interaction of the derivatives with the metallic cations at the surface, for instance Fe^{2+} . Therefore, it is to be expected that the derivatives with the most nucleophilic character will be the

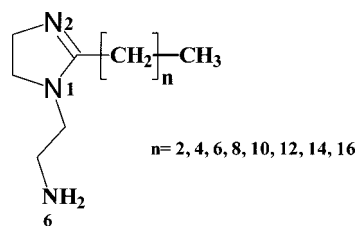


FIGURE 2. The E imidazoline derivatives, generated from the increase of size of the hydrocarbon group.

best corrosion inhibitors. It should be mentioned that we have studied these effects in the gas phase, instead of the liquid one where corrosion commonly occurs. Nevertheless, we present one case where the solvent effects are taken into account.

Some characteristics of the electronic structure were studied using natural bond orbital (NBO) [19] and Mulliken [20] population analysis, determined for each neutral and charged molecule. The details of the outermost valence electrons were obtained through the analysis of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO). Drawings of these orbitals are displayed in Figures 3(a)–3(c) for the A–I derivatives.

Results and Discussion

The calculated B3LYP/6-311G** ground-state geometries of the imidazolines derivatives studied in this work are shown in Figures 1(a)–1(c). It can be observed that, even for different attached R1 and R2 groups, the bond lengths of the structures differ by less than 0.02 Å while the internal bond angles of the imidazolinic ring are very similar for all the derivatives. For instance, the C3–N1 bond lengths fall in the 1.39–1.40 Å range, indicating the formation of a single bond between those atoms, with the C3 center having a sp^2 hybridization. On the other hand, the C3–N2 equilibrium distances are in the 1.27–1.28 Å range implying the formation of a highly localized double bond among these atoms. These results are consistent with the fact that N1 is a tertiary nitrogen atom, while N2 behaves as an iminic one. The appearance of the C3–N2 double bond in similar imidazoline compounds has been confirmed by infrared (IR) and ultraviolet (UV) spectral analysis [21], where the 1600 cm^{-1} IR vibrational mode is characteristic of the double bond of the imidazoline ring. A value of 1610 cm^{-1} for commercial imidazolines has been reported for that mode [22]. For the A, E, and F molecules the reported experimental values [23] for the C3–N2 modes are 1610, 1650, and 1665 cm^{-1} , respectively. In our calculations, that vibrational mode falls in the range $1628\text{--}1699\text{ cm}^{-1}$. The difference may arise from inaccuracies of the calculations in that we assume an harmonic model. Continuing with the description of the structural parameters for the imidazoline rings, it can be observed that in most of the molecules, the N1–C5 and N2–C4 bond lengths are equal to 1.47 Å. On the other hand, the C4–C5 distances are 1.54–1.55 Å,

meaning that C4 and C5 have typical sp^3 hybridizations. These structural parameters suggest that the N1–C3–N2 region of the ring is relatively rich in electrons, which are available for their donation to another species.

Regarding the shape of the molecules, an interesting feature is that as the size of the R2 group increases, its terminal group tends to be oriented toward the ring producing the geometries displayed in Figure 1(b). For example, in the E, F, and G molecules the N1–H7 distance is in the 2.3–2.64 Å range, which is close to a typical hydrogen bridge length. Even more, the N6–H7 distance in E and the O6–H7 separation in F are equal to 1.02 and 0.966 Å, respectively, while the S6–H7 distance in G shows a larger value of 1.35 Å, representing a weaker S–H bond. It should be noted that in G there is consistently a stronger N1–H7 (of 2.6 Å) hydrogen bond. This geometry suggests that since the bonding around the S atom is relatively weak, the electrons on the S atom may have a greater freedom for reaction with cationic species.

The Mulliken population analyses revealed that the N1, N2, and N6 nitrogen atoms (as well as Cl6 and O6, of structures H and F) have an excess electronic population, approximately 0.4 electrons, meaning that those centers are nucleophilic in their interaction with a metallic surface. However, the highest occupied molecular orbital is mainly located on N1 and N2; see Figure 3(a)–3(b). Indeed, in most of the structures the HOMO is located on N1 and N2. These features indicate that the most preferred active site, for an electrophilic attack of the imidazoline derivatives, is probably located around the region defined by the two nitrogen atoms of the ring. This is in agreement with the observed reactivity of the chemistry of the metal coordination of the imidazoline compounds [24, 25], where the metal–ligand interaction occurs through one or both of such nitrogen atoms.

In Table I we report the total energies, orbital energies for HOMO and LUMO, the $\Delta E_{\text{HOMO-LUMO}}$ gaps, and the dipole moments of the imidazoline derivatives. These parameters also give valuable information about the reactivity behavior. For example, if the $\Delta E_{\text{HOMO-LUMO}}/2$ relation is considered as the global hardness, η , the expected order of reactivity is

$$A > F > B > E > C > D > G > H > I.$$

The inconvenience of this assignment lies in the fact that, as can be observed in Table II, the hardness

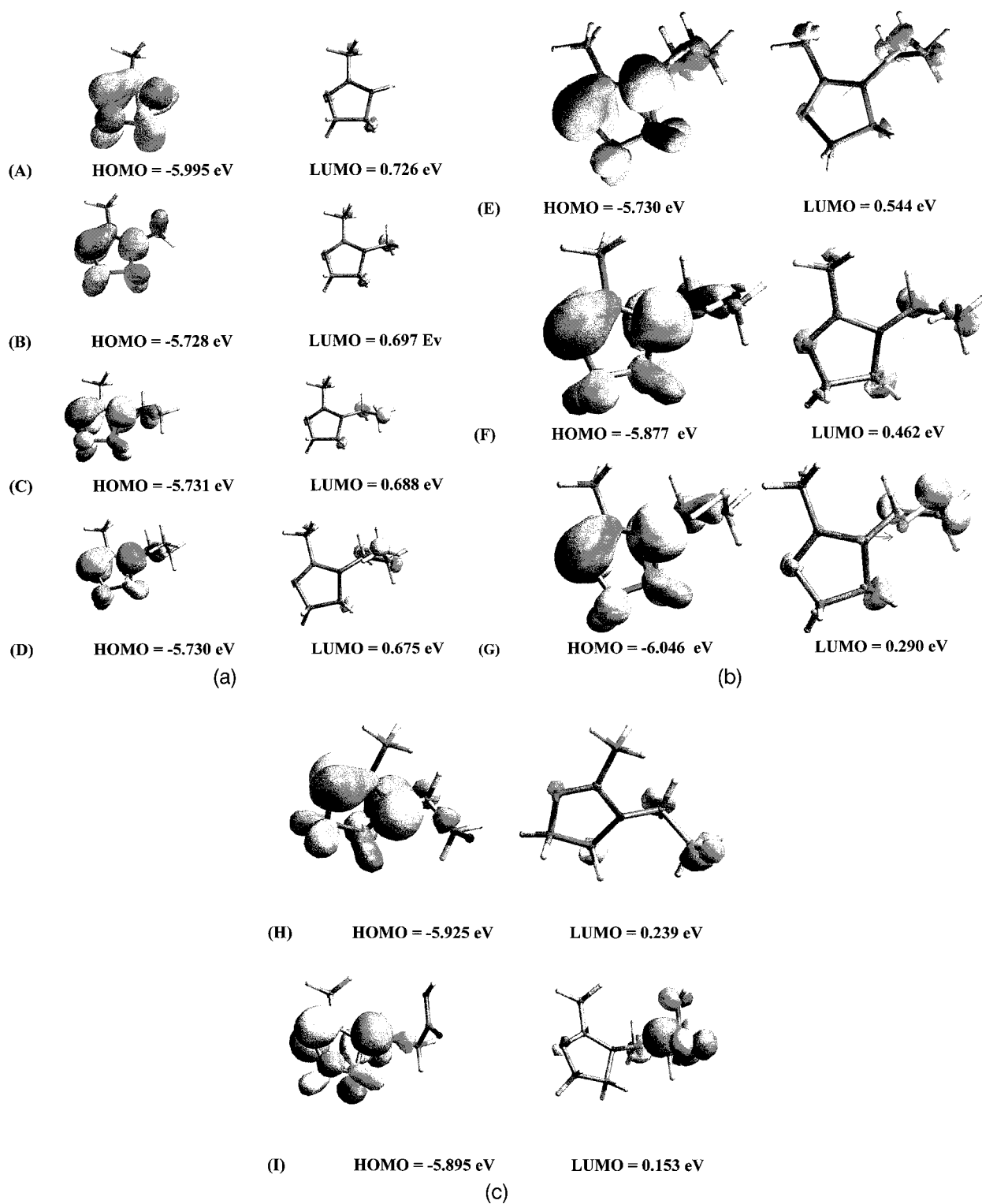


FIGURE 3. (a) Molecular orbitals HOMO and LUMO for the A, B, C, and D molecules. (b) Molecular orbitals HOMO and LUMO for the E, F, and G molecules. (c) Molecular orbitals HOMO and LUMO for the H and I derivatives.

TABLE I

Calculated B3LYP total energies, orbital energies for HOMO and LUMO, $\Delta E_{\text{HOMO-LUMO}}$, hardness, η , and dipole moments for the lowest energy states of the A-I imidazoline derivatives.

Molecule	Total energy (hartrees)	HOMO (eV)	LUMO (eV)	$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ (eV)	$\eta = \Delta E/2$ (eV)	μ (debyes)
A	-266.808	-5.995	0.726	6.720	3.360	2.7068
B	-306.125	-5.728	0.697	6.425	3.213	2.779
C	-345.453	-5.731	0.688	6.419	3.209	2.765
D	-384.776	-5.730	0.675	6.405	3.203	2.747
E	-400.813	-5.877	0.544	6.422	3.211	1.946
F	-420.687	-6.108	0.462	6.570	3.285	2.040
G	-743.665	-6.046	0.290	6.336	3.168	2.407
H	-805.072	-5.925	0.239	6.164	3.082	3.329
I	-534.076	-5.895	0.153	6.048	3.024	2.932

values exhibit a relatively small variation with R1 and R2.

To get more precise information on local reactivity, the Fukui Indices (FI) were calculated for all the

atomic sites of each of the imidazoline derivative. The Fukui analysis together with the charge distribution and global hardness, quoted above, provides a more complete scheme of the reactivity of these

TABLE II

Calculated NAO Fukui indices (FI) for the neutral and charged species of the A-I imidazoline derivatives.^a

Molecule	Atom	M-	M	M+	Fukui -	Fukui +
A	N1	-0.692	-0.663	-0.374	-0.029	-0.289
	N2	-0.601	-0.528	-0.231	-0.073	-0.297
B	N1	-0.502	-0.514	-0.216	0.011	-0.298
	N2	-0.623	-0.529	-0.252	-0.094	-0.277
C	N1	-0.512	-0.514	-0.220	0.002	-0.294
	N2	-0.629	-0.529	-0.258	-0.100	-0.271
D	N1	-0.512	-0.518	-0.223	0.006	-0.295
	N2	-0.618	-0.530	-0.262	-0.088	-0.268
E	N1	-0.519	-0.527	-0.281	0.008	-0.246
	N2	-0.618	-0.526	-0.291	-0.092	-0.235
	N6	-0.873	-0.830	-0.719	-0.044	-0.110
F	N1	-0.537	-0.542	-0.269	0.005	-0.273
	N2	-0.628	-0.520	-0.261	-0.108	-0.258
	O6	-0.766	-0.730	-0.668	-0.036	-0.062
G	N1	-0.513	-0.527	-0.298	0.014	-0.230
	N2	-0.609	-0.521	-0.295	-0.087	-0.226
	S6	-0.256	-0.062	0.153	-0.195	-0.215
H	N1	-0.502	-0.511	-0.226	0.009	-0.285
	N2	-0.619	-0.525	-0.256	-0.095	-0.269
	Cl6	-0.272	-0.087	-0.030	-0.185	-0.057
I	N1	-0.502	-0.521	-0.233	0.019	-0.288
	N2	-0.614	-0.524	-0.259	-0.091	-0.265

^a Only the highest FI values are quoted.

imidazoline derivatives. The calculated FI, for the neutral and charged derivatives, are reported in Table III. Only the largest FI values are quoted. The input charges, q , needed for the computations of the FI were obtained through the use of the natural atomic orbitals (NAO).

It was found that the largest FI values, about -0.23 and -0.29 , occur on the N1 and N2 atoms. Again, this is consistent with the observed behavior deduced from the Mulliken populations quoted above. In particular, compounds A, B, C, and D contain two nitrogen atoms, N1 and N2, but they differ by the attached R2 group to N2. Starting from A, it is observed that the replacement of H by a CH_3 group slightly increases the FI value of N1; see Table II. The replacement of H by C_2H_5 — and C_3H_7 — has no noticeable effect on the FI value of N1. Overall, in A–D, the FI of N2 is slightly smaller than that of N1. So, in A–B, the reactivity is mainly located on N1 and N2. The effect of varying the size of the hydrocarbon, R2 group, is negligible.

The compounds E, F, and G contain the NH, OH, and SH units, respectively, in the R2 group. It should be noted that, in these compounds, there is a hydrogen bridge between the H atom (of the NH, OH, and SH units) and the N1 atom of the ring. The Fukui analysis indicates that for E the N6 has a FI value of -0.11 , meaning that its reactivity is significant, although smaller than that of N1 and N2. In compound F, the O6 site has a relatively low FI value and consequently a low reactivity. However, in the derivative G, the S6 atom is seen to be as reactive as N1 and N2 since its FI value, -0.21 , is comparable to that of the N atoms. So, these results predict that compound G, as yet not reported in the literature, may present an enhanced behavior in its reactivity or anticorrosion behavior since it may be able to bind to a metallic surface through the N1, N2, and S6 sites simultaneously. It is important to note that in G the S6–H7, 1.35 \AA , and the C–S6, 1.83 \AA , bond lengths are relatively long, reflecting the fact that the electrons in S6 are more able to interact with a metallic cation. Similarly, the structural features around S6 promote the existence of a relatively strong S6–H7–N1 hydrogen bond. The correlation of this property with reactivity or anticorrosion behavior is suggested by these results and indicates the type of imidazoline derivatives that should be synthesized to achieve a high yield in the inhibition of

corrosion. The FI values of the N1, N2, N6, and S6 atomic sites are given in Table II.

The derivatives H and I contain the Cl atom and the COOH group, respectively, on R2. The Fukui analysis indicates that Cl produces a very small effect on the reactivity of N1 and N2, which have FI values of about -0.29 and -0.27 , respectively, whereas the Cl center has a low FI value of -0.057 . Moving to compound I, the oxygen atoms of the —COOH group have very small FI values, of -0.003 and -0.04 . Therefore, the carboxylate group does not play an important role in the reactivity of I, whose nitrogen atoms have FI values of -0.29 and -0.27 , similar to the other compounds. These results indicate that the inclusion of the Cl and —COOH moieties do not render a substantial improvement of the reactivity properties of the imidazoline derivatives.

On the other hand, for the E derivatives it was observed that the FI values for N1, N2, and N6 have little sensitivity with respect to the increasing size of the R1 chain; see Figure 2 and Table III. It can be seen that the N1 and N2 show FI values ranging from -0.23 up to -0.25 , while N6 reaches a maximum FI value of about 0.10 . This picture is uniform for all of the E derivatives. This means that their local reactivity is approximately the same. In this case, the relevant role of R1 in the reactivity properties, related with corrosion inhibition, is mainly determined by the partition coefficient from density functional theory (DFT) calculations [26].

In summary, the Fukui analysis for imidazoline derivatives indicates that E, F, and G exhibit the highest reactivity, making them promising species for the inhibition of corrosion. However, the corrosion phenomenon is carried out in the liquid phase. Therefore, solvent effects need to be taken into account on the geometrical and electronic properties of the derivatives. Structural relaxation subject to solvent effects were carried out for compound E. For this purpose we have used the polarizable continuum model (PCM) approach [27] recently implemented in Gaussian 98. It is important to mention that to achieve convergence, the PCM calculations need to be performed in combination with the DIIS (discrete iterative interpolation scheme) option [28]. In this way, the gas-phase optimized structure of E was reoptimized in the liquid phase using the B3LYP/6-31G* method. The solvent parameters, including the dielectric constant, were the same as

TABLE III
Calculated NAO Fukui indices for the neutral and charged species of the E derivatives.^a

Molecule	Atom	M ⁻	M	M ⁺	Fukui ⁻	Fukui ⁺
E	N1	-0.519	-0.527	-0.281	0.008	-0.246
	N2	-0.618	-0.526	-0.291	-0.092	-0.235
	N6	-0.873	-0.830	-0.719	-0.044	-0.110
<i>n</i> = 2	N1	-0.508	-0.516	-0.268	0.007	-0.248
	N2	-0.576	-0.528	-0.294	-0.047	-0.234
	N6	-0.867	-0.827	-0.718	-0.040	-0.110
<i>n</i> = 4	N1	-0.510	-0.516	-0.267	0.005	-0.249
	N2	-0.590	-0.528	-0.294	-0.062	-0.234
	N6	-0.863	-0.827	-0.720	-0.036	-0.107
<i>n</i> = 6	N1	-0.513	-0.515	-0.267	0.002	-0.249
	N2	-0.591	-0.529	-0.294	-0.063	-0.235
	N6	-0.860	-0.827	-0.721	-0.033	-0.106
<i>n</i> = 8	N1	-0.510	-0.515	-0.267	0.005	-0.248
	N2	-0.582	-0.529	-0.294	-0.053	-0.235
	N6	-0.864	-0.827	-0.721	-0.037	-0.106

^a Only the highest FI values are shown.

those implemented for water ($\epsilon = 78.39$) in the Gaussian 98 program. It was found that the solvent effects produced relatively small changes in the bond lengths and bond angles of E. The most noticeable change was the reduction of the N1-H7 distance, which goes from 2.64 Å in the gas phase to 2.55 Å in the liquid. Therefore, at least for compound E, the gas-phase optimized structure is quite similar to that in the liquid phase.

Finally, to obtain more information about the relationship between the reactivity and the inhibition of corrosion properties, we have studied the interaction of the high reactive derivative E with an iron oxide surface. The infinite surface was modeled using an Fe(OH)₃(H₂O)₃ finite cluster, which has bond lengths and bond angles as that reported for the surface [24]. The interaction of E with this cluster was studied by means of all-electron calculations using the B3LYP/6-31G* method. Note that due to computational requirements a smaller basis was employed. The Fe(OH)₃(H₂O)₃ cluster may be considered as a minimal model of the iron oxide surface. When E approaches the surface, a water molecule is released leaving room for the coordination of the metallic Fe site with the active site of E. As stated above, the highest active sites of E are the nitrogen atoms, N1 and N2. For this rea-

son we have analyzed two reaction modes for the E-Fe(OH)₃(H₂O)₂ system, and they are shown in Figure 4. The one labeled as A responds to the approach of N1 to the Fe atom; while B is of the N2-Fe interaction. Final optimized geometries of A and B are shown in Figure 4. Although the Fe-O distances were relaxed, they experience only very small changes of about 0.01 Å, with respect to those of the surface. The lowest energy coordination mode is B, while A was found 17 kcal/mol of higher energy. The Fe-N1 distance in A is equal to 2.23 Å, but in B the Fe-N2 distance has a short value of 1.96 Å. For example, in bare Fe-N2 [29], the Fe-N distances are 1.71 and 1.81 Å. That is, the Fe-N2 separation for B reflects a relatively strong E-surface interaction and indicates that E has been chemisorbed on the surface, providing corrosion protection.

Conclusions

A theoretical reactivity study was performed for a series of imidazoline derivatives containing different hydrocarbon, R1, and pendant, R2, groups. The Fukui indices calculated by means of the B3LYP functional indicate that the reactivity of these derivatives is located mainly on the nitrogen atoms of

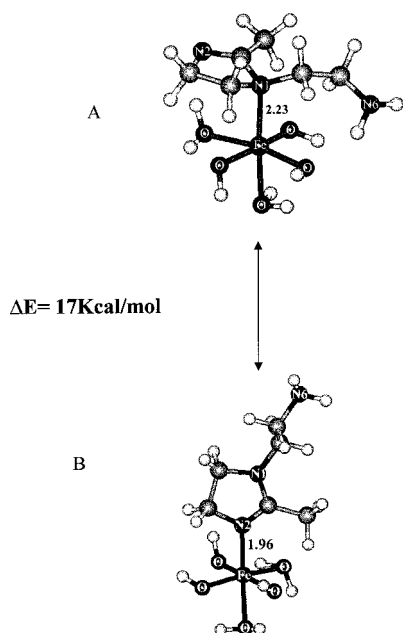


FIGURE 4. Lowest energy coordination modes for the E-Fe(OH)₃(H₂O)₂ system. The Fe-N distances are indicated in angstroms.

the imidazoline ring. The results indicate that E, F, and G derivatives are the most promising ones for the inhibition of corrosion, since they have the NH, OH, and SH units attached at R2. In particular, in G the sulfur atom is as reactive as N1 and N2. That is, when R2 contains the —SH moiety, the FI sulfur value is enhanced, with the N1 and N2 FI values showing similar magnitudes. Overall, the FI results indicate that an electrophilic reaction may be expected to occur preferentially on the N1 and N2 sites of the imidazolinic ring and on the sulfur site of the pendant group. The charge distribution analysis of the HOMO levels is in agreement with this behavior. Varying the pendant R2 group does not alter the reactivity of the N1 and N2 atoms of the heterocycle, despite the strong variation in electronegativity of these mobile groups. Similarly the size of the hydrocarbon R1 chain attached to C2 does not greatly modify the observed reactivity of the corresponding derivatives.

The effects of the solvent on the ground-state geometry were taken into account for E, and the results indicate that the gas-phase optimized structure of E is quite similar to that in the liquid phase. To obtain more information about the reactivity and the inhibition of corrosion properties the interaction of the high reactive derivative E with an iron oxide surface was analyzed. The results show that E can

be strongly bonded to the surface, and may be able to provide effective corrosion protection.

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References

1. Lakeland Laboratories Limited, Peel Lane, Astley Green, Tyldesley, Manchester, M29 7FE, England.
2. Hoffman, K. *The Chemistry of Heterocyclic Compounds*; Interscience: New York, 1953; Chapter VII, pp. 213–245.
3. (a) Patai, S. *The Chemistry of the Carbonyl Group*; Wiley: New York, 1996; Vol. 1, pp. 177–210. (b) Bistline, Jr., R. G.; Hampson, J. W.; Linfield, W. M. *J Am Chem Soc* 1983, 60, 823.
4. Sastri, V. S. *Corrosion Inhibitors, Principles and Application*; Wiley: New York, 1998.
5. Durnie, W.; De Marco, R.; Jefferson, A.; Kinsella, B. *J Electrochem Soc* 1999, 146, 1751–1756.
6. Lukovits, I.; Bak , I.; Shaban, A.; K lm n, E. *Electrochim Acta* 1998, 43, 131–136.
7. Yang, W.; Mortier, W. J. *J Am Chem Soc* 1986, 108, 5708.
8. Fukui, K.; Yonesawa, T.; Shingu, H. *J Chem Phys* 1952, 20, 722–725.
9. (a) Parr, R. G.; Yang, W. J. *J Am Chem Soc* 1984, 106, 4049. (b) Yang, W. J.; Parr, R. G. *Proc Natl Acad Sci USA* 1985, 82, 6723.
10. Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz, Jr., J. L. *Phys Rev Lett* 1982, 49, 1691.
11. Michalak, A.; De Proft, F.; Geerlings, P.; Nalewajski, R. F. *J Phys Chem A* 1999, 103, 762–771, and references therein.
12. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98 (Revision A.7)*; Gaussian: Pittsburgh, 1998.
13. Lee, C.; Yang, W.; Parr, R. G. *Phys Rev B* 1988, 37, 785.

14. Becke, A. D. *J Chem Phys* 1993, 98, 5648.
15. Becke, A. D. *Phys Rev A* 1988, 38, 3098.
16. McLean, A. D.; Chandler, G. S. *J Chem Phys* 1980, 72, 5639.
17. Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J Chem Phys* 1980, 72, 650.
18. Foresman, J. B.; Frisch, A. E. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian: Pittsburgh, 1995; Chapter 7; p. 158.
19. Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem Rev* 1988, 88, 899.
20. Mulliken, R. S. *J Chem Phys* 1955, 23, 1833.
21. Wang, D.; Li, S.; Ying, Y.; Wang, M.; Xiao, H.; Chen, Z. *Corrosion Sci* 1999, 41, 1911–1919.
22. Martin, J. A.; Valone, F. W. *Corrosion* 1985, 41, 281–287.
23. Sadtler Research Laboratories, Inc., Subsidiary of Block Engineering, Inc., Philadelphia, 1976.
24. Ramachandran, S.; Tsai, B.-L.; Blanco, M.; Chen, H.; Tang, Y.; Goddard, III, W. A. *J Phys Chem A* 1997, 101, 83–89, and references therein.
25. Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; Saunders, Inc.: Philadelphia, 1977.
26. Ramachandran, S.; Tsai, B.-L.; Blanco, M.; Chen, H.; Tang, Y.; Goddard, III, W. A. *Langmuir* 1996, 12, 6419–6428.
27. Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *J Chem Phys Lett* 1996, 255, 327.
28. Pomelli, C.; Tomasi, J.; Barone, V. *Theor Chem Acc* 2001, 105, 446.
29. Zacarías, A.; Torrens, H.; Castro, M. *Int J Quantum Chem* 1997, 61, 467.