Corrosion inhibitors part 3[1]: quantum chemical studies on the efficiencies of some aromatic hydrazides and Schiff bases as corrosion inhibitors of steel in acidic medium

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Abstract

A quantum chemical study of the efficiency of some *o*-, *m*-, and *p*-substituted benzohydrazides, cinnamohydrazide, and Schiff bases derived from salcylaldehyde with o-substituted anilines, *p*-substituted benzaldehydes with 2-aminopyridine and 2-aminopyrimidine, benzaldehyde and cinnamaldehyde with *p*-phenylenediamine as corrosion inhibitors of steel in the presence of 1M HCl is presented. The AM1, PM3, MINDO/3 and MNDO semi-empirical SCF molecular orbital methods were used. A possible correlation between corrosion inhibition efficiencies and structural properties was searched to reduce the number of compounds to be selected for testing from a library of compounds. Quantum parameters, total negative charge (*TNC*) on the molecule, energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), dipole moment (μ), total energy (*TE*), and linear solvation energy terms, molecular volume (*Vi*) and dipolar-polarization (π^*) were correlated to corrosion inhibition efficiency of the studied compounds. The results were used to predict the corrosion inhibition of some related aromatic hydrazide derivatives with correlation coefficient $r > 0.96$.

Keywords: Corrosion inhibition, hydrazide, Schiff base, AM1, PM3, MINDO/3, MNDO

Introduction

The dissolution rate of steel during cleaning, pickling, and scaling etching is quite high in acidic medium; the inhibition of such dissolution may be achieved with organic compounds containing π electrons and/or hetero atoms (i.e. N, O and S) which can be adsorbed on the metal surface.[1–15] The effect of concentration, functional groups and halide ions of quaternary ammonium inhibitors as well as the effect of N- and S-containing organic compounds such as substituted

benzothiazoles and various organic S-containing compounds on the corrosion of iron and steel have been studied.[2,3,8] The inhibition efficiency of 3,5-bis(*N*-dihydropyridyl)-4-amino-1,2,4-triazoles,[6] thiophenol, phenol and aniline,[9] 2,5-bis(*N*-dihydropyridyl)-1,3,4-thiadiazole,[10] 2,5-bis(4-dimethylaminophenyl)-1,3,4-thiadiazole,[11] 2-mercaptothiazoline, cetyl pyridinium chloride[12] and heterocyclic anils has been reported.[13–15]

The efficiency of an organic inhibitor of metallic corrosion does not only depend on the structural characteristics of the inhibitor but also on the nature of the metal and environment. The selection of a suitable inhibitor for a particular system is a difficult task because of the selectivity of the inhibitors and a wide variety of environments.

Quantitative structure activity relationship (QSAR) has been the subject of intense interest in medicinal chemistry, but to a less extent in the field of corrosion.[3,16–38] For the development of new corrosion inhibitors, the aim of this work is to correlate the structural characteristics of hydrazides and Schiff bases with their corrosion inhibition efficiency at different inhibitor concentrations in aqueous acid solutions. The development of equations for calculating the corrosion inhibition efficiency may lead to a prediction of the efficiency of some inhibitors; this should enable the selection of compounds for tests from a large number of compounds that can be developed by the concept of combinatorial chemistry and constructed compound libraries. To this end, the relation between the inhibition efficiency and quantum chemical calculation parameters, E_{HOMO}, E_{LUMO}, dipole moment, total negative charge on molecules, and linear solvation energy relationship was investigated.

Methods of calculations

Quantum calculations were carried out using Restricted Hartree-Fock (RHF) level and AM1, PM3, MNDO and MINDO/3 semi-empirical SCF-MO methods in the MOPAC 2000 program of CS ChemOffice packet program version 8 for Windows.[39] Calculations were performed on an IBM compatible Intel Pentium IV 2.8 GHz computer. All quantum theoretical calculations were starting without any geometry constraints for full geometry optimizations using the program default calculation setting. The following quantum chemical indices, depending on the try and error in the SPSS program in solving the non-linear equations were considered: the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the dipole moment (μ), total negative charge (*TNC*) and total energy (*TE*) on the molecule, as well as the linear solvation energy relationships (LSER) parameters, intrinsic molecular volume (*Vi*) and dipolar-polarizability factor (π^*).[40–42] Statistical analyses were performed using SPSS program version 10.0 for Windows. Non-linear regression analyses were performed by unconstrained sum of squared residuals for loss function and estimation methods of Levenberg-Marquardt using SPSS program version 10.0 for Windows.

Results and Discussion

Hydrazides **1**–**4** and Schiff bases **5**–**18** (Figure 1) have been reported as corrosion inhibitors for steel in acidic medium, with inhibition efficiencies expressed as E_{exp} (%) based on the weight loss method for compounds **1**–**4**,[43] **5**–**7**,[44] **8**–**10**,[45] **11**–**13**[46] and **14**–**18**.[47]

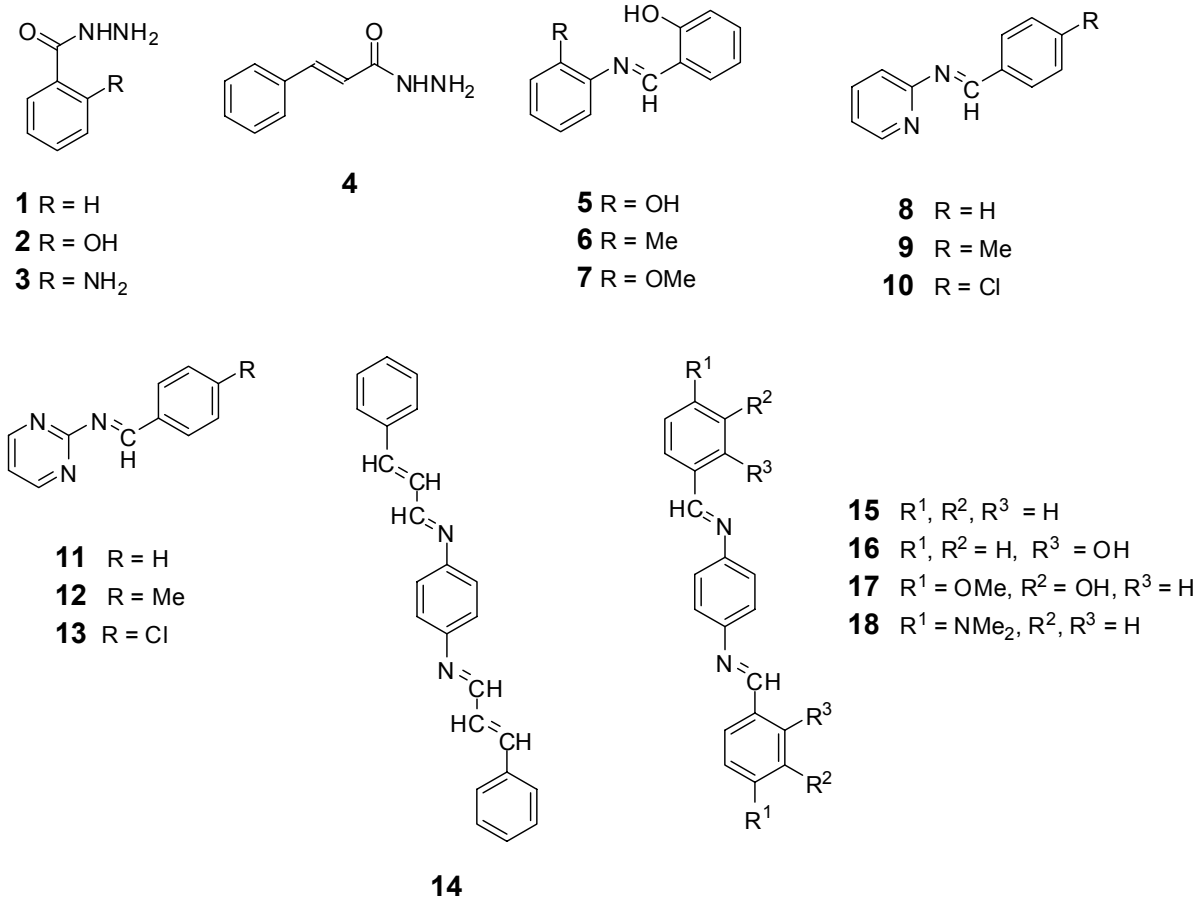

Figure 1

Quantum chemical parameters of compounds **1**–**18** (Table 1), E_{HOMO} (eV), E_{LUMO} (eV), μ (Debye), *TNC* and *TE* (eV), linear solvation energy parameters (LSER), the intrinsic (van der Waals) molecular volume *Vi* (cm^3/mole) and dipolar-polarizability term (π^*) in the LSER model, were used to scale the solute electrostatic stabilization of molecular charge by using methods of Hickey and Passino-Reader [19].

The correlation analysis between quantum parameters E_{HOMO}, E_{LUMO}, μ, *TE,* and *Vi* and E_{exp} (%) for compounds **1**–**18** shows significant correlations ($p<0.001$). The inhibition efficiency increases if the compound can donate electrons from its HOMO to the LUMO of the metal, whereby chelation on the metal surface occurs. Thus, the inhibition increases with increasing values of E_{HOMO} and μ, and decreasing values of E_{LUMO}. The highest value of E_{HOMO} was found

for compound **14**, which also exhibits the best corrosion inhibition efficiency. However, a low corrosion inhibition efficiency is generally due to low E_{HOMO} and high E_{LUMO} values, which were not applicable in the case of hydrazides **1**–**3**. On the other hand, compounds with high values of *Vi* and π^* such as compounds **14**–**18** show high corrosion inhibition efficiencies (Table 1 and 2).

Table 1. Quantum chemical parameters of compounds **1** to **18** in gas phase using AM1, PM3, MINDO/3 and MNDO semi-empirical calculation and LSER parameters (*Vi*, π^*) calculation

Comp. No.	*Vi*	π^*	E_{HOMO}	E_{LUMO}	μ	*TNC*	*TE*
AM1							
1	82.26	1.43	-10.166	-0.243	3.867	-1.564	-1739.6
2	77.79	1.56	-9.150	-0.079	3.933	-1.843	-2060.1
3	80.59	1.56	-8.734	-0.079	1.837	-1.984	-1960.8
4	99.03	1.53	-9.178	-0.427	2.905	-1.836	-2022.7
5	112.45	1.74	-8.729	-0.541	2.083	-1.865	-2662.3
6	118.05	1.57	-8.812	-0.632	0.804	-1.795	-2497.6
7	122.06	1.74	-8.809	-0.617	1.315	-1.916	-2817.6
8	110.58	1.76	-9.123	-0.790	3.043	-1.430	-2085.9
9	120.20	1.72	-8.988	-0.762	3.033	-1.558	-2241.8
10	114.46	1.88	-9.168	-0.963	3.556	-1.339	-2446.0
11	103.30	1.76	-9.349	-0.933	1.924	-1.435	-2150.8
12	112.92	1.72	-9.168	-0.912	1.846	-1.563	-2306.7
13	111.65	1.88	-9.360	-1.090	2.797	-1.343	-2510.9
14	218.84	2.57	-7.855	-1.545	3.386	-2.743	-3755.7
15	168.35	2.37	-8.466	-1.020	2.419	-2.154	-3192.0
16	176.36	2.63	-8.557	-0.839	3.722	-2.636	-3833.3
17	203.59	2.89	-8.410	-0.849	6.279	-2.812	-4785.0
18	265.18	2.67	-8.090	-0.926	2.370	-2.939	-4255.0
PM3							
1	82.26	1.43	-9.750	-0.287	3.587	-1.023	-1569.6
2	77.79	1.56	-9.127	-0.372	3.785	-1.387	-1863.4
3	80.59	1.56	-8.911	-0.139	1.901	-1.075	-1747.6
4	99.03	1.53	-9.226	-0.673	3.257	-1.253	-1837.0
5	112.45	1.74	-8.694	-0.741	2.591	-1.615	-2458.1
6	118.05	1.57	-8.783	-0.886	1.263	-1.445	-2313.7
7	122.06	1.74	-8.723	-0.811	0.634	-1.616	-2607.1
8	110.58	1.76	-9.175	-0.894	3.054	-1.093	-1898.7
9	120.20	1.72	-9.023	-0.874	2.982	-1.136	-2048.4
10	114.46	1.88	-9.081	-1.024	3.532	-1.096	-2200.1
11	103.30	1.76	-9.296	-1.081	2.085	-1.049	-1926.9
12	112.92	1.72	-9.125	-1.048	1.860	-1.100	-2076.7
13	111.65	1.88	-9.164	-1.183	2.901	-1.050	-2228.4
14	218.84	2.57	-7.942	-1.712	3.098	-2.251	-3470.6
15	168.35	2.37	-8.735	-1.058	2.471	-1.718	-2938.2
16	176.36	2.63	-8.557	-0.839	3.722	-2.636	-3833.3
17	203.59	2.89	-8.480	-1.039	5.364	-2.294	-4411.5
18	265.18	2.67	-8.102	-1.010	2.401	-1.959	-3890.7
MINDO/3							
1	82.26	1.43	-9.041	0.666	4.114	-0.846	-1701.4
2	77.79	1.56	-8.773	0.624	3.287	-1.680	-2013.6
3	80.59	1.56	-7.955	0.798	2.882	-1.406	-1909.1
4	99.03	1.53	-8.896	0.393	3.789	-0.907	-1984.1
5	112.45	1.74	-7.393	0.846	1.707	-1.734	-2625.4
6	118.05	1.57	-7.505	0.747	1.059	-1.544	-2469.9

7	122.06	1.74	-7.632	0.776	1.239	-1.945	-2781.2
8	110.58	1.76	-7.581	0.726	1.559	-0.922	-2052.2
9	120.20	1.72	-7.587	0.581	1.551	-1.004	-2208.9
10	114.46	1.88	-7.701	0.213	1.643	-1.278	-2384.9
11	103.30	1.76	-7.704	0.534	0.906	-1.206	-2103.3
12	112.92	1.72	-7.708	0.389	0.920	-1.295	-2260.0
13	111.65	1.88	-7.802	0.009	2.116	-1.485	-2435.9
14	218.84	2.57	-6.914	-0.457	2.742	-0.891	-3714.2
15	168.35	2.37	-7.625	0.037	1.027	-0.804	-3153.2
16	176.36	2.63	-6.785	0.565	2.464	-2.431	-3777.9
17	203.59	2.89	-6.982	0.548	5.040	-3.325	-4713.4
18	265.18	2.67	-7.530	0.015	0.998	-1.988	-4191.4
MNDO							
1	82.26	1.43	-9.913	-0.372	3.733	-1.114	-1743.6
2	77.79	1.56	-9.044	-0.057	2.881	-1.432	-2066.1
3	80.59	1.56	-9.229	-0.271	2.769	-1.398	-1965.4
4	99.03	1.53	-9.405	0.099	3.018	-1.199	-2027.2
5	112.45	1.74	-8.629	-0.739	2.427	-1.340	-2667.9
6	118.05	1.57	-8.783	-0.675	0.593	-1.161	-2502.0
7	122.06	1.74	-8.464	-0.778	1.522	-1.446	-2823.7
8	110.58	1.76	-8.979	-0.806	2.814	-1.000	-2088.1
9	120.20	1.72	-8.946	-0.831	2.822	-1.002	-2244.7
10	114.46	1.88	-9.154	-1.049	3.824	-1.007	-2428.7
11	103.30	1.76	-9.236	-0.929	1.743	-1.296	-2153.4
12	112.92	1.72	-9.205	-0.906	1.787	-1.294	-2310.0
13	111.65	1.88	-9.439	-1.138	3.208	-1.307	-2494.0
14	218.84	2.57	-7.824	-1.513	3.423	-1.520	-3757.7
15	168.35	2.37	-8.384	-0.954	2.225	-1.314	-3194.7
16	176.36	2.63	-8.337	-0.986	3.500	-1.972	-3839.5
17	203.59	2.89	-8.746	-0.263	5.580	-2.179	-4796.6
18	265.18	2.67	-8.206	-0.887	2.250	-2.468	-4261.9

Compared to compounds **5**–**7** the effectiveness of compound **14** as corrosion inhibitor may be attributed to the presence of an additional C=C double bond in conjugation with the aromatic ring and the C=N bond in **14**. Similarly, compound **4** is a more effective inhibitor than **2** and **3** due to the additional C=C double bond. This may play a major role in increasing molecular adsorption to the metal surface due to the π-electron delocalization extending over the aromatic ring, the C=C, and C=O or C=N double bonds in **4** and in **14**, respectively.

Although a number of satisfactory correlations[48–57] have been reported for the inhibition efficiency of various inhibitors and selected quantum chemical parameters, no simple relation or direct trend relationship can be derived for such classes of inhibitors. A non-linear regression analysis was used to correlate quantum chemical parameters (E_{HOMO}, E_{LUMO}, μ, TE), LSER (Vi, π^*) and inhibitor concentrations (C_i) with the experimental inhibition efficiencies obtained by weight loss methods for compounds **1**–**18**. Thus, a composite index of more than one quantum parameter, which might affect the inhibition efficiency of molecules was correlated with the experimental corrosion inhibition efficiencies.

The nonlinear equation was derived from the linear model,[57] which approximates the corrosion inhibitor efficiency (E_{cal} %):

E_{cal} (%) = $Ax_jC_i + B$ (1)

A and B are constants obtained by regression analysis; x_j is a quantum chemical index characteristic for the molecule j; C_i denotes the experiment's concentration. Equation 1 was used to derive equation 2, which is the non-linear model (NLM) proposed by Lukovits and co-worker[58] for studying the interaction of corrosion inhibitors with metal surfaces in acidic medium.

$$E_{cal}(\%) = \frac{(Ax_i + B)C_i}{1 + (Ax_i + B)C_i} \times 100 \quad (2)$$

In the non-linear method of analysis, multiple regressions were performed on inhibition efficiencies of compounds **1**–**18** at a concentration range from 0.07 to 10.0 mM (Table 2). Non-linear equations 3 and 4 were obtained for AM1, where x_j is a composite index of selected quantum chemical parameters E_{HOMO}, E_{LUMO}, μ, *TNC*, π* and *Vi* in equation 3, and E_{HOMO}, E_{LUMO}, μ, *TNC*, π* and *Vi* in equation 4. Calculated efficiencies from such equations at different concentrations of compounds **1**–**18** illustrate good correlation with experimental efficiencies (E_{exp} %) with correlation coefficients r = 0.976 and 0.9696, respectively.

The non-linear model equations 5 and 6 proposed for PM3 on compounds **1**–**18** shows correlation coefficients between E_{exp} (%) and E_{cal} (%), r = 0.9696 and 0.9691. The x_j represents a composite index of selected quantum parameters E_{HOMO}, E_{LUMO}, μ, π* and *Vi* in equation 5 and E_{HOMO}, E_{LUMO}, μ and *Vi* in equation 6.

The non-linear model for MINDO/3 is represented in equation 7 with correlation coefficient r = 0.9752 between the E_{exp} (%) and E_{cal} (%), where x_j is the quantum parameters E_{HOMO}, E_{LUMO}, μ, *TE*, *TNC*, π* and *Vi*. Regression analysis for the quantum parameter obtained by MNDO calculation leads to propose the non-linear equations 8 and 9 with correlation coefficient, r = 0.9771 and 0.977, respectively between E_{exp} (%) and E_{cal} (%). The x_j in both equations is the quantum parameters E_{HOMO}, E_{LUMO}, μ and *TNC* as well as LSER parameter *Vi*.

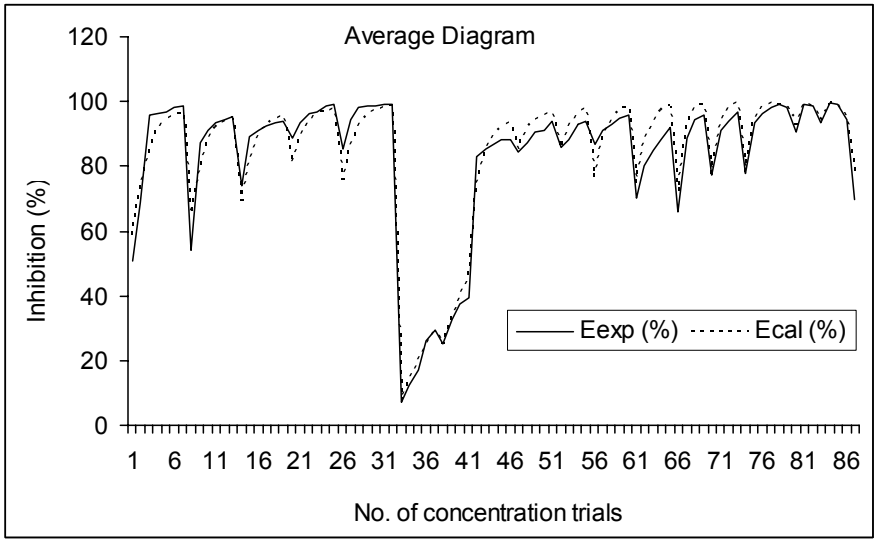

Figure 2. Diagram of average calculated efficiencies obtained by equations 3–9 and experimental efficiencies at different concentrations of compounds **1**–**18**.

Figure 2 shows a typical pattern of average E_{cal} (%) obtained from the seven proposed equations 3–9 and the E_{exp} (%) obtained by weight loss for compounds **1**–**18**[43–47] at different concentrations. The average of E_{cal} (%) obtained for each concentration is correlated with the E_{exp} (%) with correlation coefficient r = 0.9784 (Figure 3) with standard deviations ranging from ±0.02 to ±7.44. Moreover, the standard deviations between the E_{cal} obtained from different proposed model are ranged from ±0.19 to ±8.63 (Table 2). The high correlation coefficients (r ~ 0.97) obtained from the seven proposed QSAR equations 3–9 are strong evidence for the participation of quantum parameters E_{HOMO}, E_{LUMO}, dipole moment, *TE* and LSER in the inhibition efficiency of compounds **1**–**18**.

Table 2. Experimental inhibition efficiency obtained using weight loss of compounds **1**–**18** and calculated inhibition efficiency obtained by the proposed equations for AM1, PM3, MINDO/3 and MNDO semiempirical calculation

No.	Conc. [mM]	E_{exp} (%)	E_{cal} (%): AM1	PM3		MINDO/3	MINDO		Average	ST 1	ST 2
			Eq. 3	Eq. 4	Eq. 5	Eq. 6	Eq. 7	Eq. 8	Eq. 9			
1	0.73	83.2	76.00	74.81	73.65	73.74	74.51	72.54	76.96	74.60	6.08	1.50
	1.47	85.3	86.36	85.59	84.83	84.89	85.39	84.09	86.98	85.45	0.10	0.98
	2.20	86.8	90.48	89.91	89.35	89.39	89.76	88.80	90.93	89.80	2.12	0.72
	2.94	88.4	92.68	92.24	91.79	91.83	92.12	91.36	93.04	92.15	2.65	0.57
	3.67	88.0	94.06	93.69	93.32	93.35	93.60	92.96	94.35	93.62	3.97	0.47
2	0.66	7.30	6.57	8.28	7.25	7.86	7.62	7.37	9.04	7.71	0.29	0.79
	1.31	12.3	12.32	15.30	13.52	14.57	14.16	13.73	16.58	14.31	1.42	1.36
	1.97	17.3	17.41	21.32	18.99	20.37	19.83	19.27	22.97	20.02	1.93	1.78
	2.63	26.1	21.94	26.54	23.82	25.43	24.81	24.14	28.45	25.02	0.76	2.08
	3.29	29.4	26.00	31.11	28.10	29.89	29.20	28.46	33.20	29.42	0.02	2.30
3	1.32	25.2	23.49	25.71	24.53	24.64	25.47	24.73	25.88	24.92	0.20	0.83
	1.98	32.8	31.54	34.17	32.77	32.90	33.89	33.01	34.37	33.24	0.31	0.99
	2.65	37.6	38.05	40.90	39.39	39.53	40.60	39.65	41.12	39.89	1.62	1.07
	3.31	39.5	43.43	46.38	44.83	44.97	46.08	45.09	46.61	45.34	4.13	1.11
4	0.62	84.2	90.38	85.33	86.02	86.22	91.03	75.60	81.88	85.21	0.71	5.26
	1.23	87.1	94.95	92.08	92.49	92.60	95.30	86.10	90.03	91.94	3.42	3.13
	1.85	90.4	96.57	94.58	94.86	94.94	96.82	90.29	93.13	94.46	2.87	2.22
	2.47	91.0	97.41	95.88	96.10	96.16	97.60	92.53	94.76	95.77	3.38	1.72
	3.08	93.8	97.92	96.68	96.85	96.90	98.07	93.94	95.76	96.59	1.97	1.41
5	0.5	86.0	84.02	84.02	84.72	84.82	84.29	89.15	90.68	85.95	0.03	2.76
	1.0	88.0	91.31	91.31	91.73	91.78	91.47	94.26	95.11	92.43	3.13	1.57
	2.5	93.0	96.33	96.33	96.52	96.54	96.40	97.62	97.98	96.82	2.70	0.68
	5.0	94.0	98.13	98.13	98.23	98.24	98.17	98.80	98.98	98.38	3.10	0.35
6	0.2	87.0	77.36	74.74	79.07	79.17	74.08	73.89	78.90	76.74	7.25	2.44
	0.5	91.0	89.52	88.09	90.43	90.48	87.72	87.62	90.34	89.17	1.29	1.32
	1.0	93.0	94.47	93.67	94.97	95.00	93.46	93.40	94.92	94.27	0.90	0.74
	2.5	95.0	97.71	97.37	97.93	97.94	97.28	97.25	97.91	97.63	1.86	0.32
	5.0	96.0	98.84	98.67	98.95	98.96	98.62	98.61	98.94	98.80	1.98	0.16
7	0.2	70.0	73.61	71.70	80.11	79.59	67.94	74.37	77.80	75.02	3.55	4.44
	0.5	80.0	87.46	86.37	90.97	90.70	84.12	87.88	89.75	88.18	5.78	2.48
	1.0	85.0	93.31	92.69	95.27	95.12	91.37	93.55	94.60	93.70	6.15	1.41
	2.5	88.0	97.21	96.94	98.05	97.99	96.36	97.32	97.77	97.38	6.63	0.61

	5.0	92.0	98.59	98.45	99.02	98.98	98.15	98.64	98.87	98.67	4.72	0.31
8	1.0	90.4	90.68	93.60	94.33	94.01	84.80	95.81	96.52	92.82	1.71	3.99
	5.0	98.3	97.99	98.65	98.81	98.74	96.54	99.13	99.28	98.45	0.11	0.94
	10.0	99.0	98.98	99.32	99.40	99.37	98.24	99.56	99.64	99.22	0.15	0.48
9	1.0	93.5	93.29	94.13	93.95	93.94	93.21	96.15	96.81	94.50	0.70	1.41
	5.0	98.5	98.58	98.77	98.73	98.73	98.56	99.21	99.35	98.85	0.24	0.31
	10.0	99.3	99.29	99.38	99.36	99.36	99.28	99.60	99.67	99.42	0.08	0.15
10	0.2	69.7	68.61	77.07	77.97	76.68	82.53	83.82	85.90	78.94	6.53	5.79
	1.0	94.4	91.62	94.38	94.65	94.27	95.94	96.28	96.82	94.85	0.32	1.74
	5.0	98.9	98.20	98.82	98.88	98.80	99.16	99.23	99.35	98.92	0.02	0.38
	10.0	99.5	99.09	99.41	99.44	99.40	99.58	99.62	99.67	99.46	0.03	0.19
11	0.2	65.9	74.67	75.80	83.05	81.55	65.82	60.56	65.33	72.40	4.59	8.63
	1.0	88.8	93.65	94.00	96.08	95.67	90.59	88.48	90.41	92.70	2.75	2.90
	5.0	94.2	98.66	98.74	99.19	99.10	97.96	97.46	97.92	98.43	2.99	0.66
	10.0	95.9	99.33	99.37	99.59	99.55	98.97	98.71	98.95	99.21	2.34	0.33
12	0.2	77.1	79.25	77.55	82.46	81.49	77.88	75.97	70.58	77.88	0.55	3.93
	1.0	91.1	95.02	94.53	95.92	95.65	94.62	90.65	92.31	94.10	2.12	1.92
	5.0	93.7	98.96	98.86	99.16	99.10	98.88	97.98	98.36	98.76	3.57	0.43
	10.0	96.9	99.48	99.42	99.58	99.55	99.44	98.98	99.17	99.37	1.75	0.22
13	0.2	77.8	75.97	78.54	82.59	81.16	85.04	70.97	73.34	78.23	0.31	5.10
	1.0	93.3	94.05	94.82	95.96	95.56	96.60	92.44	93.22	94.66	0.96	1.51
	5.0	96.1	98.75	98.92	99.16	99.08	99.30	98.39	98.57	98.88	1.97	0.33
	10.0	98.2	99.37	99.46	99.58	99.54	99.65	99.19	99.28	99.44	0.88	0.17
14	0.07	85.21	79.22	70.71	71.11	71.40	82.06	77.75	80.37	76.09	6.45	4.87
	0.15	94.48	88.41	82.84	83.11	83.31	90.15	87.48	89.11	86.35	5.75	3.15
	0.30	98.02	93.85	90.62	90.78	90.90	94.82	93.32	94.24	92.65	3.80	1.82
	0.59	98.45	96.83	95.08	95.17	95.23	97.34	96.55	97.04	96.17	1.61	0.98
	0.89	98.83	97.86	96.66	96.72	96.77	98.21	97.67	98.00	97.41	1.00	0.67
	1.19	99.19	98.39	97.48	97.52	97.56	98.65	98.24	98.50	98.05	0.81	0.51
	1.49	99.26	98.71	97.97	98.01	98.04	98.92	98.59	98.79	98.43	0.59	0.41
15	0.18	88.84	72.47	75.70	81.27	80.51	87.68	84.11	86.52	81.18	5.42	5.56
	0.35	93.43	84.04	86.17	89.67	89.20	93.44	91.37	92.77	89.52	2.76	3.43
	0.70	96.31	91.33	92.57	94.55	94.29	96.61	95.49	96.25	94.44	1.32	1.93
	1.06	96.85	94.05	94.92	96.30	96.12	97.71	96.95	97.47	96.22	0.45	1.34
	1.41	98.54	95.47	96.14	97.20	97.06	98.27	97.69	98.09	97.13	1.00	1.02
	1.76	99.13	96.34	96.89	97.75	97.64	98.61	98.15	98.47	97.69	1.02	0.83
16	0.16	74.18	67.50	64.83	71.77	70.79	60.70	74.04	75.68	69.33	3.43	5.30
	0.32	89.02	80.59	78.67	83.56	82.89	75.55	85.09	86.16	81.79	5.11	3.75
	0.63	91.2	89.25	88.06	91.05	90.65	86.07	91.94	92.57	89.94	0.89	2.30
	0.95	92.71	92.57	91.71	93.85	93.56	90.26	94.48	94.92	93.05	0.24	1.65
	1.26	93.62	94.32	93.65	95.31	95.09	92.51	95.80	96.14	94.69	0.76	1.28
	1.58	93.98	95.41	94.86	96.21	96.04	93.92	96.61	96.89	95.70	1.22	1.05
17	0.13	54.13	62.66	62.61	68.87	68.62	64.35	64.50	65.76	65.34	7.92	2.57
	0.27	87.14	77.04	77.00	81.56	81.39	78.31	78.42	79.35	79.01	5.75	1.87
	0.53	90.98	87.03	87.01	89.85	89.74	87.83	87.90	88.48	88.26	1.92	1.16
	0.80	93.43	90.97	90.95	92.99	92.92	91.55	91.60	92.02	91.85	1.11	0.84
	1.06	94.41	93.07	93.05	94.65	94.59	93.52	93.56	93.89	93.76	0.46	0.66
	1.33	95.54	94.38	94.36	95.67	95.63	94.75	94.78	95.05	94.95	0.42	0.54
18	0.07	50.75	57.01	61.38	63.19	65.85	58.16	51.74	55.45	58.97	5.81	4.83
	0.13	68.92	72.62	76.07	77.44	79.41	73.55	68.20	71.34	74.09	3.65	3.83
	0.27	95.59	84.14	86.41	87.29	88.52	84.76	81.09	83.27	85.07	7.44	2.54

0.54	96.51	91.39	92.71	93.21	93.91	91.75	89.56	90.87	91.91	3.25	1.49
0.81	96.76	94.09	95.02	95.37	95.86	94.34	92.79	93.73	94.46	1.63	1.05
1.08	98.02	95.50	96.22	96.49	96.86	95.70	94.49	95.22	95.78	1.58	0.81
1.35	98.6	96.37	96.95	97.17	97.47	96.53	95.54	96.14	96.60	1.42	0.66

Average: The average of the calculated inhibition efficiency obtained by the proposed models; ST 1: standard deviation between the experimental inhibition efficiency obtained by weight loss and average of the calculated inhibition efficiency obtained by the proposed equations ST 2: standard deviation between the results obtained by the proposed equations

AM1 Models

$$E_{cal}\% = \frac{(0.003 \times E_{HOMO} - 48.51 \times E_{LUMO} + 2.08 \times \mu - 32.4 \times TNC - 42.76 \times \pi^* - 0.034 \times Vi - 2.22) \times C_i}{1 + (0.003 \times E_{HOMO} - 48.51 \times E_{LUMO} + 2.08 \times \mu - 32.4 \times TNC - 42.76 \times \pi^* - 0.034 \times Vi - 2.22) \times C_i} \times 100 \quad (3)$$

$$E_{cal}\% = \frac{(1.72 \times E_{HOMO} - 19.56 \times E_{LUMO} + 0.442 \times \mu - 14.95 \times \pi^* + 0.119 \times Vi + 26.66) \times C_i}{1 + (1.72 \times E_{HOMO} - 19.56 \times E_{LUMO} + 0.442 \times \mu - 14.95 \times \pi^* + 0.119 \times Vi + 26.66) \times C_i} \times 100 \quad (4)$$

PM3 Models

$$E_{cal}\% = \frac{(-8.35 \times E_{HOMO} - 20.62 \times E_{LUMO} - 3.5 \times \mu + 5.2 \times \pi^* + 0.054 \times Vi - 82.84) \times C_i}{1 + (-8.35 \times E_{HOMO} - 20.62 \times E_{LUMO} - 3.5 \times \mu + 5.2 \times \pi^* + 0.054 \times Vi - 82.84) \times C_i} \times 100 \quad (5)$$

$$E_{cal}\% = \frac{(-6.79 \times E_{HOMO} - 18.51 \times E_{LUMO} - 2.98 \times \mu + 0.104 \times Vi - 65.55) \times C_i}{1 + (-6.79 \times E_{HOMO} - 18.51 \times E_{LUMO} - 2.98 \times \mu + 0.104 \times Vi - 65.55) \times C_i} \times 100 \quad (6)$$

MINDO/3 Model

$$E_{cal}\% = \frac{(6.77 \times E_{HOMO} - 33.25 \times E_{LUMO} - 0.0443 \times TE + 21.67 \times TNC - 33.08 \times \pi^* - 0.327 \times Vi + 104.5) \times C_i}{1 + (6.77 \times E_{HOMO} - 33.25 \times E_{LUMO} - 0.0443 \times TE + 21.67 \times TNC - 33.08 \times \pi^* - 0.327 \times Vi + 104.5) \times C_i} \times 100 \quad (7)$$

MNDO Models

$$E_{cal}\% = \frac{(12.41 \times E_{HOMO} - 6.42 \times E_{LUMO} + 3.18 \times \mu + 27.68 \times TNC + 0.164 \times Vi + 129.71) \times C_i}{1 + (12.41 \times E_{HOMO} - 6.42 \times E_{LUMO} + 3.18 \times \mu + 27.68 \times TNC + 0.164 \times Vi + 129.71) \times C_i} \times 100 \quad (8)$$

$$E_{cal}\% = \frac{(14.27 \times E_{HOMO} - 6.03 \times E_{LUMO} + 3.12 \times \mu + 35.51 \times TNC + 0.214 \times Vi + 154.08) \times C_i}{1 + (14.27 \times E_{HOMO} - 6.03 \times E_{LUMO} + 3.12 \times \mu + 35.51 \times TNC + 0.214 \times Vi + 154.08) \times C_i} \times 100 \quad (9)$$

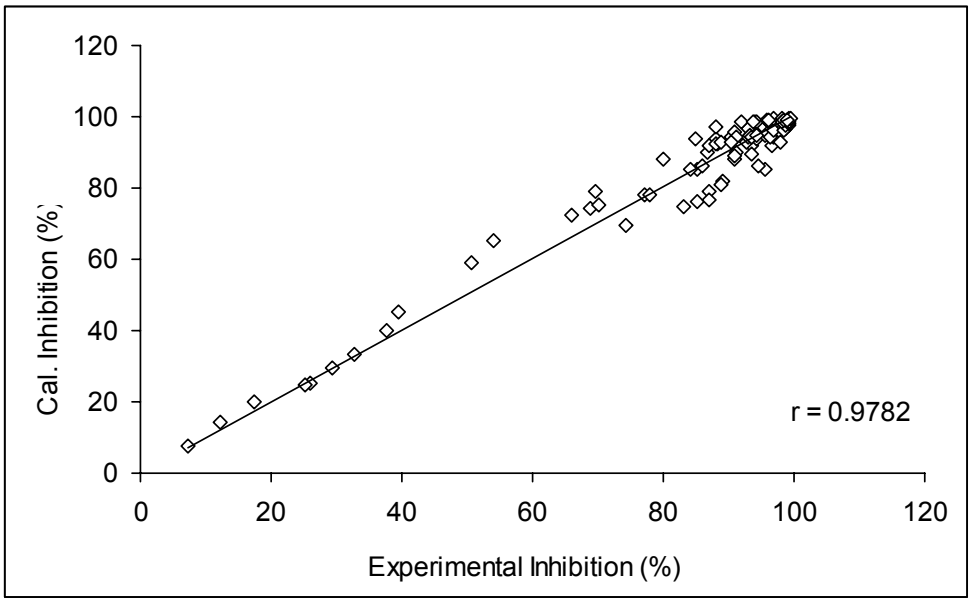

Figure 3. Plot of average calculated efficiencies obtained by Eq. 3–9 versus experimental efficiencies of compounds **1**–**18**.

A higher value of E_{HOMO} of the inhibitor indicates the ability of the molecules to offer electrons to *d* orbitals of metallic steel and a higher inhibition efficiency of the inhibitor for steel in acidic medium. The negative coefficients of E_{LUMO} in equations 3–9 indicate that *d* orbitals of steel donate electrons to the *d* orbital of the Schiff bases leading to the presence of a feed back bond. The presence of feed back bonds leads to an increased chemical adsorption of inhibitor molecules at the steel surface, thus increasing the inhibition efficiency of these compounds (Tables 1 and 2).

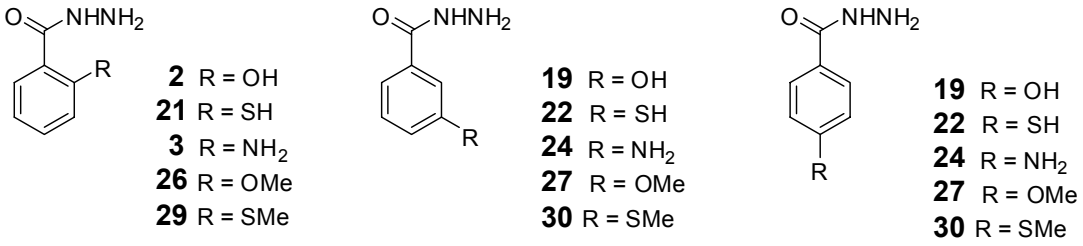

Figure 4

The above calculations prompted us to evaluate the results in a method for predicting the corrosion inhibition of some analogues of hydrazides **1**–**3** in order to reduce the number of tested compounds for inhibition efficiency. Consequently, the inhibition efficiency can be treated as a controlled property via the change of electronic properties of compounds by changing their functional groups. Thus, 14 proposed hydrazides **19**–**31** (Figure 4) were subjected to similar

methods of quantum calculations (Table 3). The seven proposed models (Eqs. 3–9) were applied at concentration ranges from 0.2 to 1.0 (Table 4). All seven equations give a high corrosion inhibition for the 14 proposed compounds with average inhibitions fluctuating between 30.25 to 95.36% and standard deviations ranged from ±1.9 to ±16.7 (Table 4). Changing the position of the OH group in compound **2** to *m*- and *p*-positions as in **19** and **20**, respectively, leads to a decrease of E_{HOMO} and E_{LUMO} values and increases E_{cal} (%). On the other hand, replacing the OH group in hydrazide **2** by SH (**21**) shows an increase of the calculated inhibition efficiency. In addition, changing the substitution position from *o*-SH to *m*- and *p*-SH increases the inhibition efficiency even more, and replacing SH by SMe gives a higher inhibition efficiency. However, introducing OMe at *o*-, *m*- and *p*- positions of **1** as in compounds **26–28** shows not much of a change of the average E_{cal} (%) (Table 2 and 4). The average E_{cal} (%) obtained for compounds **19–31** using equations 3–9 is decreased in the following order: **23** > **29** > **19** > **30** > **27** > **22** > **20** > **26** > **31** > **28** > **21** > **24** > **25**.

Electron-donating substituents at the aromatic rings of the studied compounds increases the basicity of nitrogen atoms and hence increases its proton affinity and charge. Thus by making suitable substitutions in the parent inhibitor molecule an improvement in the degree of corrosion inhibition was achieved.

Table 3. Quantum chemical parameters of proposed compounds **19–31** in gas phase using AM1, PM3, MINDO/3 and MNDO semiempirical calculation

Comp. No.	*Vi*	π^*	E_{HOMO}	E_{LUMO}	μ	*TNC*	*TE*
AM1							
19	77.79	1.56	-9.501	-0.350	1.696	-1.756	-2060.3
20	77.79	1.56	-9.522	-0.299	2.245	-1.791	-2060.3
21	84.94	1.94	-8.653	-0.686	2.452	-1.640	-1934.1
22	84.94	1.94	-8.708	-0.718	1.859	-1.632	-1934.1
23	84.94	1.94	-8.783	-0.821	2.102	-1.640	-1934.1
24	80.59	1.56	-8.956	-0.119	3.797	-1.866	-1960.6
25	80.59	1.56	-8.870	-0.101	3.820	-1.922	-1960.8
26	87.40	1.62	-9.193	0.197	2.793	-1.820	-2215.1
27	87.40	1.62	-9.088	0.058	3.078	-1.772	-2215.3
28	87.40	1.62	-9.503	-0.198	4.500	-1.816	-2215.5
29	94.55	1.85	-8.443	-0.269	2.616	-2.041	-2089.6
30	94.55	1.85	-8.469	-0.318	2.904	-2.030	-2089.8
31	94.55	1.85	-8.536	-0.409	4.070	-2.037	-2089.8
PM3							
19	77.79	1.56	-9.546	-0.552	1.442	-1.236	-1863.5
20	77.79	1.56	-9.543	-0.481	2.272	-1.287	-1863.6
21	84.94	1.94	-8.595	-0.554	3.153	-1.092	-1755.5
22	84.94	2.04	-9.034	-0.706	1.687	-1.058	-1755.8
23	84.94	2.04	-9.098	-0.805	1.345	-1.064	-1755.8
24	80.59	1.56	-9.020	-0.221	3.491	-1.074	-1747.6
25	80.59	1.56	-8.478	-0.190	4.609	-1.158	-1747.4
26	87.40	1.62	-9.193	0.197	2.793	-1.820	-2215.1
27	87.40	1.62	-9.552	-0.285	2.961	-1.205	-2012.5
28	87.40	1.62	-9.569	-0.218	3.947	-1.227	-2012.5
29	94.55	1.85	-9.305	-0.718	2.879	-1.233	-1905.1

30	94.55	1.85	-8.903	-0.426	2.325	-1.271	-1905.2
31	94.55	1.85	-8.928	-0.529	3.689	-1.273	-1905.2
MINDO/3							
19	77.79	1.56	-8.695	0.574	2.548	-1.470	-2013.6
20	77.79	1.56	-8.617	0.784	3.467	-1.686	-2013.6
21	84.94	1.94	-8.303	0.410	2.413	-1.224	-1933.7
22	84.94	1.94	-8.671	0.434	2.495	-1.068	-1933.7
23	84.94	1.94	-8.325	0.421	3.393	-1.217	-1933.7
24	80.59	1.56	-7.951	0.810	4.730	-1.186	-1909.0
25	80.59	1.56	-7.922	0.914	4.827	-1.393	-1909.1
26	87.40	1.62	-9.193	0.197	2.793	-1.820	-2215.1
27	87.40	1.62	-8.661	0.610	3.690	-1.660	-2169.6
28	87.40	1.62	-8.615	0.815	4.400	-1.877	-2169.5
29	94.55	1.85	-8.931	0.141	3.653	-1.263	-2090.2
30	94.55	1.85	-8.563	0.152	2.941	-1.144	-2090.2
31	94.55	1.85	-8.561	0.146	4.159	-1.291	-2090.2
MNDO							
19	77.79	1.56	-9.294	-0.341	1.848	-1.379	-2066.3
20	77.79	1.56	-9.354	-0.308	2.915	-1.467	-2066.3
21	84.94	1.94	-9.814	-0.632	2.807	-1.189	-1972.5
22	84.94	1.94	-9.175	-0.457	1.702	-1.242	-1972.5
23	84.94	1.94	-9.224	-0.565	2.335	-1.247	-1972.5
24	80.59	1.56	-9.215	-0.368	3.438	-1.331	-1965.3
25	80.59	1.56	-9.208	-0.492	3.816	-1.444	-1965.2
26	87.40	1.62	-9.317	-0.085	2.073	-1.412	-2222.1
27	87.40	1.62	-9.405	-0.120	4.215	-1.350	-2222.1
28	87.40	1.62	-9.379	-0.365	4.099	-1.510	-2222.0
29	94.55	1.85	-9.755	-0.654	3.779	-1.207	-2129.0
30	94.55	1.85	-9.809	-0.654	4.266	-1.289	-2129.0
31	94.55	1.85	-9.826	-0.769	2.256	-1.227	-2129.0

Table 4. Calculated inhibition efficiency [E_{cal} (%)] for compounds **19**–**31** obtained by the proposed models for AM1, PM3, MINDO/3 and MNDO semiempirical calculation.

Comp	Conc.	E_{cal} (%):		PM3		MINDO/3	MNDO		Average	STDEV
No	[mM]	Eq. 3	Eq. 4	Eq. 5	Eq. 6	Eq. 7	Eq. 8	Eq. 9		
19	0.20	53.67	43.43	75.62	72.63	57.80	46.38	47.46	56.71	12.8
	0.60	77.66	69.72	90.30	88.84	80.43	72.18	73.04	78.88	8.1
	0.80	82.25	75.43	92.54	91.39	84.57	77.57	78.32	83.15	6.7
	1.00	85.28	79.33	93.94	92.99	87.26	81.22	81.87	85.98	5.8
20	0.20	52.99	38.00	69.00	65.46	33.19	57.04	59.33	53.57	13.4
	0.60	77.17	64.77	86.98	85.04	59.85	79.93	81.40	76.45	10.3
	0.80	81.84	71.03	89.90	88.35	66.53	84.16	85.37	81.02	8.9
	1.00	84.93	75.40	91.76	90.45	71.30	86.91	87.94	84.10	7.8
21	0.20	40.50	59.60	44.33	33.28	26.96	27.89	33.99	38.08	11.4
	0.40	57.65	74.68	61.43	49.93	42.47	43.61	50.73	54.36	11.3
	0.60	67.12	81.57	70.49	59.94	52.55	53.71	60.70	63.73	10.2
	0.80	73.13	85.51	76.10	66.61	59.62	60.74	67.32	69.86	9.1
	1.00	77.29	88.06	79.92	71.38	64.86	65.91	72.02	74.21	8.2
22	0.20	41.22	60.51	66.69	71.71	37.83	42.86	51.45	53.18	13.3
	0.40	58.38	75.39	86.81	83.52	53.54	60.00	67.94	69.37	12.9
	0.60	67.79	82.13	90.80	88.38	63.63	69.23	76.07	76.86	10.6
	0.80	73.72	85.97	92.94	91.02	70.67	75.00	80.91	81.46	8.8
	1.00	77.81	88.45	94.27	92.69	65.85	78.95	84.12	83.16	9.9

23	0.20	64.96	65.87	80.17	76.13	33.14	53.35	58.52	61.73	15.7
	0.40	78.76	79.42	88.99	86.45	47.58	69.58	73.84	74.94	13.8
	0.60	84.76	85.27	92.38	90.54	57.45	77.43	80.89	81.25	11.7
	0.80	88.12	88.53	94.18	92.73	64.63	82.06	84.95	85.03	9.9
	1.00	90.26	90.61	95.29	94.10	70.08	85.11	87.59	87.58	8.5
24	0.20	28.47	21.61	22.42	22.57	46.46	50.09	52.40	34.86	14.1
	0.60	54.42	45.26	46.43	46.65	72.25	75.07	76.76	59.55	14.5
	0.80	61.42	52.44	53.61	53.83	77.63	80.06	81.49	65.78	13.4
25	0.20	37.41	19.12	22.20	28.62	18.84	44.27	41.29	30.25	10.7
	0.60	64.20	41.49	46.12	54.60	41.04	70.44	67.85	55.11	12.5
	0.80	70.51	48.59	53.30	61.59	48.14	76.06	73.78	61.71	11.9
26	0.40	83.20	74.15	71.78	69.25	83.03	39.53	51.02	67.42	16.4
	0.60	88.13	81.14	79.23	77.16	88.01	49.51	60.97	74.88	14.4
	0.80	90.83	85.16	83.57	81.83	90.73	56.66	67.56	79.48	12.7
	1.00	92.53	87.76	86.41	84.92	92.44	62.04	72.25	82.62	11.3
27	0.40	86.68	79.01	69.06	66.00	58.78	62.25	64.27	69.43	9.9
	0.60	90.71	84.95	77.00	74.44	68.14	71.21	72.96	77.06	8.0
	0.80	92.87	88.27	81.70	79.52	74.04	76.73	78.25	81.62	6.7
	1.00	94.21	90.39	84.80	82.91	78.09	80.48	81.81	84.67	5.7
28	0.40	83.75	70.81	50.34	47.54	80.82	50.48	44.72	61.21	16.7
	0.60	88.54	78.44	60.32	57.62	88.60	60.46	51.78	69.39	15.4
	0.80	91.15	82.91	66.96	64.44	91.20	67.09	58.87	74.66	13.4
	1.00	92.80	85.84	71.70	69.38	92.83	71.82	64.15	78.36	11.9
29	0.20	34.70	38.03	73.70	70.91	74.30	58.20	61.49	58.76	16.5
	0.40	51.52	55.10	84.86	82.98	85.25	73.58	76.15	72.78	14.0
	0.60	61.45	64.80	89.37	87.97	89.66	80.69	82.73	79.52	11.7
	0.80	68.00	71.05	91.81	90.70	92.04	84.78	86.46	83.55	10.0
	1.00	72.65	75.42	93.34	92.42	93.53	87.44	88.87	86.24	8.7
30	0.20	51.22	45.01	56.78	53.27	79.28	52.66	53.73	55.99	10.9
	0.60	75.90	71.06	79.76	77.37	91.99	76.94	77.70	78.68	6.5
	0.80	80.77	76.60	84.01	82.01	93.87	81.65	82.29	83.03	5.3
	1.00	84.00	80.36	86.79	85.07	95.03	84.76	85.31	85.90	4.5
31	0.20	71.09	55.59	45.19	42.57	56.41	31.98	30.40	47.61	14.5
	0.40	83.10	71.45	62.25	59.72	66.63	42.04	46.63	61.69	14.1
	0.60	88.06	78.97	71.21	68.98	80.67	55.81	56.72	71.49	12.1
	0.80	90.77	83.35	76.74	74.78	92.83	52.99	63.60	76.44	14.4
	1.00	92.48	86.22	80.48	78.75	94.18	58.49	68.60	79.89	12.8

Conclusions

A comparison of the inhibition effectiveness of some hydrazides and Schiff bases indicates that their inhibition effect is closely related to orbital energies (E_{HOMO} and E_{LUMO}), dipole moment, total energy and LSER parameters *Vi* and π^*. The inhibition efficiency of the Schiff bases increases with increasing E_{HOMO} and decreasing E_{LUMO}; reverse results were obtained for the hydrazides. A composite index of more than three quantum chemical parameters and one of LSER parameter is to be included in the proposed models. A highly significant multiple correlation coefficient (r >0.96) was obtained between experimental and calculated efficiencies.
A correlation of >0.96 was found between experimental efficiencies obtained by weight loss and those calculated using seven proposed models by non-linear regression analysis from the results of semi-empirical calculation methods (AM1, PM3, MINDO/3 and MNDO). These correlations

may be useful in designing new inhibitors by selecting appropriate substituents in the parent molecules.

The QSAR approach may be used to find the optimal group of parameters that might predict the structure of a molecule suitable as an inhibitor. The quantum mechanical approach may well be able to foretell molecular structures that are better for corrosion inhibition purposes if taking into account that the effect depends only on the inhibitor molecule's properties.

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