

Molecular Ionization and Deprotonation Energies as Indicators of Functional Coating Performance

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1 Supplementary Data

1.1 Experimental determination of corrosion inhibition efficacy

For comparison with experimentally determined corrosion inhibition efficacy, the results from Harvey *et al.* are presented alongside the calculated values. Within the Harvey data set corrosion inhibition efficacy is referenced against the industrial chromate standard, with the inhibitor efficiencies calculated using the weight loss of the respective alloys in 0.1 M NaCl as a baseline as defined in reference¹:

$$I\% = \frac{w - w'}{w} \times 100 \quad (1)$$

where, $I\%$ is the inhibitor efficiency (%); w is weight loss of panels after 4 weeks immersion in 0.1 M NaCl solution alone; and w' is the weight loss of panels after 4 weeks immersion in 0.1 M NaCl + 1 mM inhibitor. Thus a compound with 0% inhibitor efficiency would show the same degree of corrosion as 0.1 M NaCl; and the inhibitor would be considered to be 100% efficient if the mass loss was equivalent to the chromate standard. Conversely, compounds with negative experimental inhibition efficacy act as a corrosion accelerator rather than as an inhibitor.

1.2 Basis set dependence

Before analysing the entire set, we first examine the uncertainties associated with the computational method using three molecules with experimentally determined IP values (Thiophenol, Pyridine, 2-mercaptobenzothiazole). It is clear from Table 1, that the calculated molecular IP values of thiophenol, pyridine and 2-mercaptobenzothiazole are basis set choice dependant. Minimal basis sets such as STO-3G seriously underestimate molecular IP, and also, to a lesser extent, the SIESTA DZP basis set; which lacks diffuse functions. It can be summarized from these results that the choice of basis set does affect molecular IP, and that introducing polarization and/or diffuse functions, can improve the numerical prediction of molecular IP. While the 6-311++G basis set does provide closely matching molecular IP energies for thiophenol and pyridine, it fails to accurately predict the molecular IP of 2-mercaptobenzothiazole (2-MBT). Considering that the 6-311++G** basis set gives results within a few percent of the experimental values for the

basis set	Thiophenol IP (eV)	Pyridine IP (eV)	2-MBT [†] IP (eV)
NIST reference	8.30 ²	9.26 ²	7.99 ²
DZP [']	7.42	8.67	7.40
STO-3G	5.99	7.80	6.02
3-21G	8.10	9.10	8.24
6-21G	8.06	9.08	8.21
6-31G	8.03	9.09	8.19
6-311G	8.18	9.24	8.33
6-311+G	8.20	9.31	8.35
6-311++G	8.20	9.31	8.35
6-31G**	7.90	9.15	7.86
6-31++G**	8.06	9.34	8.02
6-311++G**	8.09	9.38	8.05
cc-pVDZ	7.97	9.21	7.91
aug-cc-pVDZ	8.07	9.33	8.02
cc-pVTZ	8.05	9.30	7.99
aug-cc-pVTZ	8.08	9.35	8.03

Table 1 NIST IP reference and vertical IP dependance on basis set choice. ['] denotes a SIESTA calculation. [†] 2-mercaptobenzothiazole (MBT)

sub-set of molecules examined, it was selected for all future calculations.

Thiophenol and pyridine molecular IPs as calculated by SIESTA were within 11% of the NIST (eval) reference energy, Gaussian (6-311++G**) results were significantly more accurate, <3% of the reference energy. It can be generalized from the data, that with the exception of molecule 4-mercaptobenzoate, that SIESTA consistently underestimates molecular IP, as expected of a minimal basis set. This underestimation may also be related to the use of pseudopotentials in SIESTA calculations, c.f. Gaussian09 (all electron) calculations.

1.3 Small organic molecules as corrosion inhibitors

The contextual use of five selected corrosion inhibitor candidate molecules, along with their presented optimised geometries are presented below.

Molecule 1H, Thiophenol also known as benzenethiol

(C₆H₆S), is a small organic molecule which has been reported to protect iron surfaces in an acidic medium³. On AA-2024-T3 it has been experimentally determined to exhibit similar corrosion inhibition to chromate¹ and is an effective AA-2024-T3 corrosion inhibitor, featuring only a thiol functional group.

Molecule 1I, Pyridine (C₅H₅N), is commonly used as an organic solvent and is an excellent example of a terrible AA-2024-T3 corrosion inhibitor, however, as an ubiquitous organic solvent a wealth of experimental data is available for comparison, hence its inclusion. This is an excellent example of a low molecular weight molecule which is also a heterocyclic compound, and has been reported to actually accelerate corrosion for some alloy formulations¹.

Molecule 2B, Benzotriazole (C₆H₅N₃), has been reported as a very effective corrosion inhibitor on a variety of materials including AA-2024-T3¹, AA-7075-T6¹, and Cu⁴. It is a classic example of an N containing heterocyclic compound. It also finds utility as an additive in aircraft deicing and for protecting silverware during dishwashing, however it and some of its derivatives have been identified as being toxic to aquatic life⁵.

Molecule 1C, Diethyl(dithiocarbamate) (C₅H₁₀NS₂), is commonly used as a copper chelating agent when prepared as a sodium salt⁶ and has been reported to exhibit almost equivalent corrosion inhibition on both AA-2024-T3 and AA-7075-T6 alloys¹. It has established inhibition properties on cold rolled steel⁷, copper⁸, and brass⁹. This molecule is an example of a corrosion inhibitor which is a well established copper chelating agent, and incidentally occupies a relatively large volume given its molecular weight.

Molecule 1W, Mercaptopropionate (C₃H₅O₂S), was recently identified as an equivalent corrosion inhibitor to the chromate standard when assessed via mass loss measurement on AA-2024-T3¹. Within the calculated data set, this molecule is unusual as it features both a carboxylate and thiol functional groups in a linear conformation.

For these five inhibitor molecules their respective geometry, calculated bond angles and lengths are presented in Figure 1. Here, experimental bond lengths and angles were directly compared wherever possible, however in some instances where unavailable. Such values were obtained from analogue molecules, and are denoted by an asterisk eg. thiophenol Θ_{CCC} was taken from the corresponding angle in nitrobenzene. As can be seen from Figure 1, the bond lengths and angles of molecules 1H, 1I, 1C, 1W and 2B are in good agreement with experimental values¹⁰.

References

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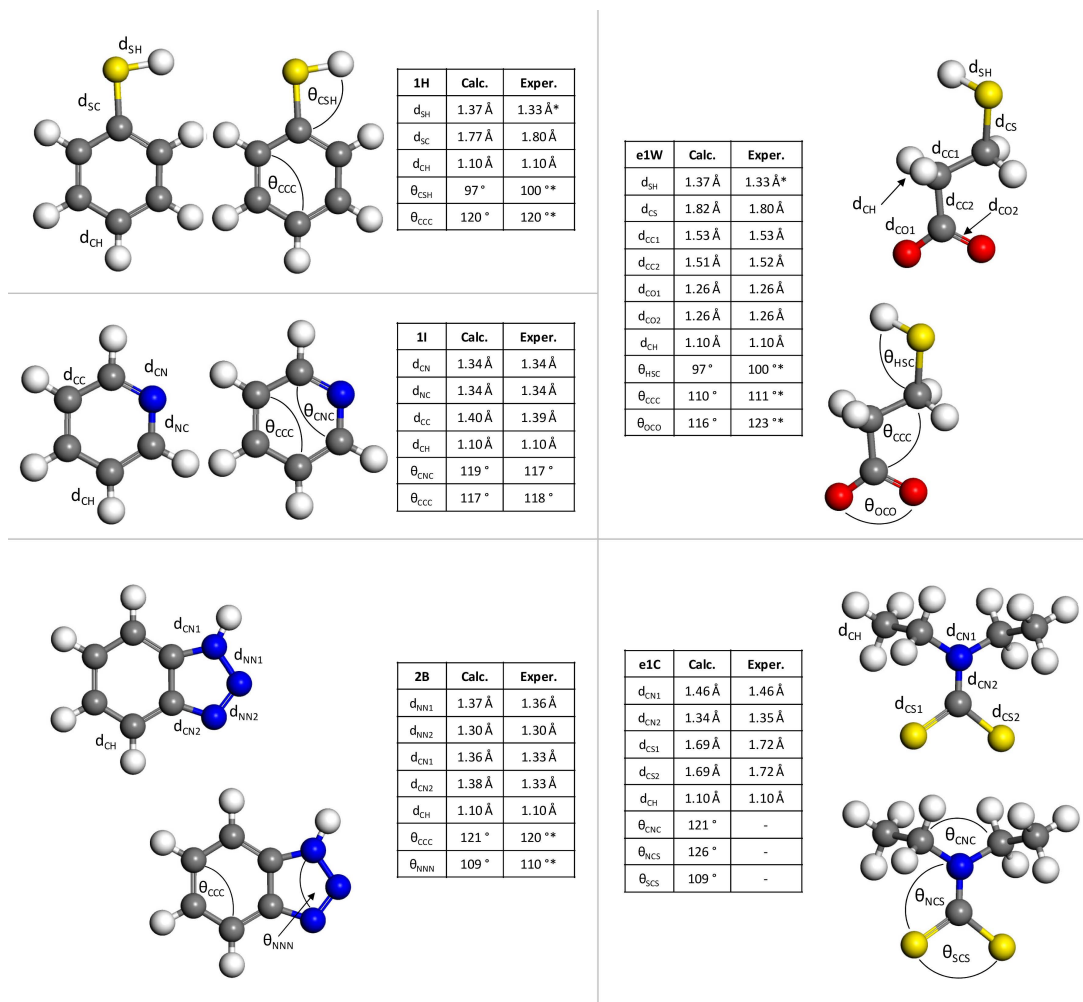


Figure 1 Comparison of bond lengths and angles of selected organic corrosion inhibitor molecules; yellow=sulphur, red=oxygen, blue=nitrogen, grey=carbon, white=hydrogen.

1.4 Adiabatic SIESTA results

ID	Molecule	IP (eV)	EA (eV)	FG (eV)	Av. DE (eV)	DE Range (eV)	Expt. (%)
1A	4,5-Diamino-2,6-dimercaptopyrimidine	6.22	-1.32	7.54	16.42	15.65 - 16.90	87 ± 0
1B	4,5-Diaminopyrimidine	6.62	-1.74	8.36	17.47	16.40 - 19.08	47 ± 3
1C	diethyl(dithiocarbamate)	6.49	0.92	5.57	16.99	16.87 - 17.09	97 ± 1
1D	2-Mercaptopyrimidine	7.84	-1.24	9.09	17.83	16.14 - 18.49	89 ± 4
1E	Pyrimidine	8.04	-1.47	9.51	18.69	18.39 - 19.00	-153 ± 1
1G	Benzoate	8.92	1.85	7.07	16.71	16.57 - 16.83	-80 ± 14
1H	Thiophenol	7.33	-1.58	8.91	18.19	16.06 - 18.80	93 ± 5
1I	Pyridine	8.21	-1.81	10.03	18.82	18.59 - 19.06	-139 ± 18
1J	4-phenylbenzoate	8.14	1.95	6.19	16.60	16.50 - 16.73	-72 ± 6
1K	4-hydroxybenzoate	8.11	1.74	6.38	16.48	15.23 - 16.93	-34 ± 5
1L	4-mercaptopbenzoate	7.76	1.88	5.87	16.27	14.76 - 16.79	97 ± 2
1M	6-mercaptopnicotinate	8.08	2.03	6.06	16.04	14.78 - 16.54	94 ± 0
1N	Nicotinate	8.39	2.05	6.34	16.40	16.23 - 16.55	-107 ± 11
1O	Isonicotinate	8.55	2.13	6.42	16.32	16.11 - 16.53	-12 ± 1
1P	Picolinate	8.52	1.72	6.80	16.63	16.46 - 16.80	58 ± 0
1Q	3-mercaptopbenzoate	7.70	1.95	5.75	16.60	16.44 - 16.76	16 ± 8
1R	Salicylate	8.13	1.58	6.55	16.54	15.10 - 17.05	-175 ± 32
1S	2-mercaptopbenzoate	7.84	2.12	5.72	16.08	14.55 - 16.61	88 ± 0
1T	2-mercaptopnicotinate	8.03	2.23	5.80	15.83	14.56 - 16.44	83 ± 2
1U	2,3-mercaptopsuccinate	6.93	2.73	4.20	14.30	13.62 - 14.81	82 ± 1
1V	Mercaptoacetate	7.42	2.07	5.35	14.97	14.76 - 15.38	96 ± 1
1W	Mercaptopropionate	8.27	1.77	6.50	15.85	15.11 - 16.08	100 ± 0
1X	Acetate	10.19	1.21	8.98	16.77	16.77 - 16.77	-12 ± 8
2A	2,5-dimercapto-1,3,4-thiadiazole	7.17	-0.94	8.11	15.42	15.40 - 15.44	26 ± 5
2B	Benzotriazole	8.24	-1.13	9.37	18.03	16.20 - 18.68	98 ± 0
2C	2-mercaptopbenzimidazole	6.90	-1.12	8.02	17.77	15.48 - 18.95	90 ± 0
2D	6-amino-2-mercaptopbenzothiazole	6.10	-1.26	7.35	17.39	15.54 - 18.48	89 ± 4
2E	2-mercaptopbenzothiazole	7.13	-0.80	7.93	17.82	15.33 - 18.66	95 ± 5

Table 2 Adiabatic molecular parameters calculated with SIESTA (DZP basis set): IP, EA, FG, DE, DE Range; experimental corrosion inhibition on AA-2024-T3 taken from reference ¹. A positive sign convention has been adopted for all DE and DE range values

**1.5 Structural representations, bond lengths
and angles of all calculated molecules**

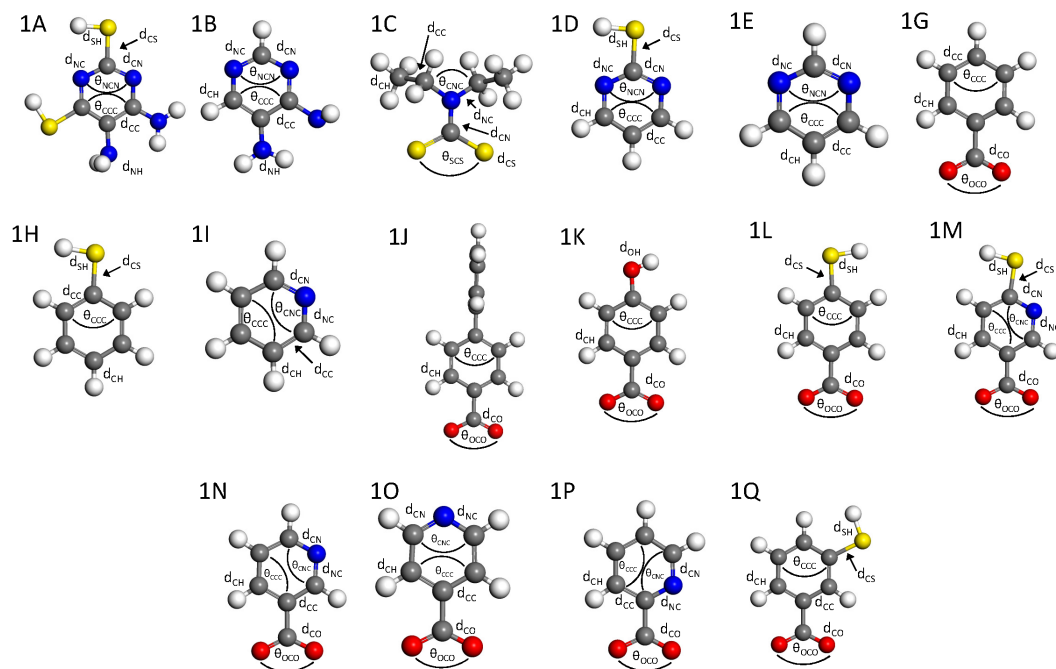


Figure 2 Structural representations of the Harvey data set, indicating bond lengths and angles of corrosion inhibitor molecules; yellow=sulphur, red=oxygen, blue=nitrogen, grey=carbon, white=hydrogen.

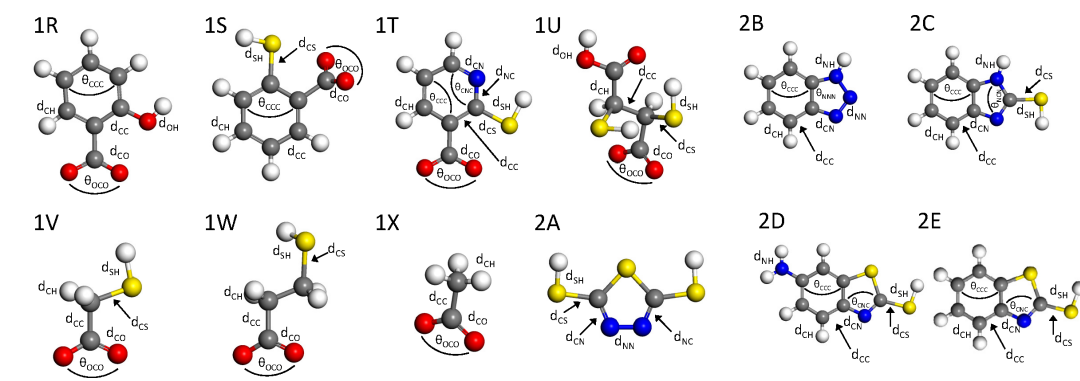


Figure 3 Structural representations of the Harvey data set, indicating bond lengths and angles of corrosion inhibitor molecules; yellow=sulphur, red=oxygen, blue=nitrogen, grey=carbon, white=hydrogen.

ID	IR	IS	IT	IU	IV	IW	IX	2A	2B	2C	2D	2E
d_{CH} (Å)	1.10	1.10	1.10	1.10	1.10	1.10	1.10	-	1.10	1.10	1.10	1.10
d_{CC} (Å)	1.41	1.39	1.41	1.53	1.52	1.53	1.52	-	1.40	1.40	1.41	1.41
d_{CO} (Å)	1.27	1.26	1.28	1.27	1.27	1.27	1.27	-	-	-	-	-
d_{CN} (Å)	-	-	1.33	-	-	-	-	1.31	1.38	1.39	1.38	1.38
d_{CS} (Å)	-	1.79	1.76	1.82	1.82	1.82	-	1.76	-	1.76	1.76	1.76
d_{NC} (Å)	-	-	1.34	-	-	-	-	1.31	-	1.32	1.30	1.30
d_{NN} (Å)	-	-	-	-	-	-	-	1.36	1.30	-	-	-
d_{NH} (Å)	-	-	-	-	-	-	-	-	1.01	1.01	1.01	-
d_{OH} (Å)	0.97	-	-	0.98	-	-	-	-	-	-	-	-
d_{SH} (Å)	-	1.38	1.38	1.38	1.37	1.37	-	1.37	-	1.37	1.37	1.37
Θ_{CCC}°	120	120	120	-	-	-	-	-	116	117	119	118
Θ_{NCN}°	-	-	-	-	-	-	-	-	-	114	-	-
Θ_{NNC}°	-	-	-	-	-	-	-	-	109	-	-	-
Θ_{CNC}°	-	-	118	-	-	-	-	-	-	-	110	-
Θ_{OCO}°	125	126	125	127	126	126	126	-	-	-	-	110

Table 4 Bond lengths and angles as calculated by SIESTA/DZP.

ID	IA	IB	IC	ID	IE	IG	IH	II	IJ	IK	IL	IM	IN	IO	IP	IQ
d_{CH} (Å)	-	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10
d_{CC} (Å)	1.42	1.42	1.52	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40
d_{CO} (Å)	-	-	-	-	-	1.27	-	-	1.27	1.28	1.27	1.27	1.27	1.27	1.26	1.27
d_{CN} (Å)	1.34	1.34	1.36	1.34	1.34	-	-	1.34	-	-	-	1.34	1.34	1.34	1.34	-
d_{CS} (Å)	1.77	-	1.73	1.77	-	-	1.77	-	-	-	1.77	1.77	-	-	-	1.77
d_{NC} (Å)	1.34	1.34	1.46	1.35	1.34	-	-	1.34	-	-	-	1.33	1.34	1.34	1.34	-
d_{NH} (Å)	1.01	1.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-
d_{OH} (Å)	-	-	-	-	-	-	-	-	0.97	-	-	-	-	-	-	-
d_{SH} (Å)	1.38	-	-	1.38	-	-	1.37	-	-	-	1.37	1.37	-	-	-	1.37
Θ_{CCC}°	115	115	-	116	116	120	120	119	119	121	120	119	118	119	118	120
Θ_{NCN}°	129	127	-	128	128	-	-	-	-	-	-	-	-	-	-	-
Θ_{CNC}°	-	-	-	117	-	-	-	117	-	-	-	117	117	117	117	-
Θ_{OCO}°	-	-	-	-	-	126	-	-	126	125	126	126	126	126	126	126
Θ_{SCS}°	-	-	-	125	-	-	-	-	-	-	-	-	-	-	-	126

Table 3 Bond lengths and angles as calculated by SIESTA/DZP.