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Molecular Design and Dynamic Simulations of Some Novel Antioxidant Lubricant Additives

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Abstract. The growing concern among chemical industrialist and other researchers to explore other alternatives to replace the long-time use of ZDDP has continued to generate momentum. Less efficiency of catalytic converters and exhaust particulate zinc matter deposit have all been traced to the frequent use of ZDDP as a base oil additive. Quantitative structure-property relationship (QSPR) and a dynamics molecular simulation were theoretical tools used for designing and investigating new antioxidant lubricant additives. Five new oxidant resistance lubricant additives were designed from the information derived from the QSPR mathematical model's high coefficient molecular descriptors. All the novel antioxidant lubricant additives properties were found to be better than our previous study, with the lubricant additive (Z)-3-(4-(5-amino-1-phenyl-1H-pyrazole-3-yl)-3,5-dimethylphenyl)-2-phenyl-5-(thiophen-2-ylmethylene)-3,5-dihydro-4H-imidazol-4-one found to possess excellent antioxidant properties of 0.850281T.A.V 0.1g/L than its co-additives. All the designed additives do not contain Phosphorus and Zinc which often rendered exhaust pipe catalytic converter inactive thereby increasing environmental pollution.Moreover, from our dynamic simulation study, all the designed additives were found to dynamically bind to the simulated surface of steel than to DLC crystal simulated surface. This research has provided a theoretical framework towards synthesizing new and better antioxidant lubricating base oil additives that could hinder the base oil from undergoing a complete circle of oxidation.

Keywords: *QSPR;* Novel *lubricant additive: DLC: DFT: Molecular dynamics simulations.*

1 .Introduction

The growing concern among chemical industrialist and other researchers to explore other alternatives to replace the long-time use of zinc dialkyl dithiophosphates (ZDDPs) has continued to generate momentum [1-8]. Recent studies show that higher concentrations (≥1800 ppm) of ZDDP with the lubricating oil has been reported to be responsible for fewer corrosion inhibitors

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efficiency [1], while less concentration of this additive has been reported to be responsible for engine failure [2]. Moreover, less efficiency of catalytic converters and exhaust particulate matter zinc deposit have all been traced to the frequent use of ZDDP as base oil additive [2].

At an elevated dynamic temperature in the internal combustion engines, the metals such as iron, zinc, copper and their alloys were reported to act as a catalyst for auto-oxidation of any form of lubricating oil. Also, the auto-oxidized lube oil often resulted in an unexpected rise in viscosity, sludge and its volume generally varnishes [4-8].Antioxidant additives are lubricating oil additives designed to hinder the base oil from undergoing a complete circle of oxidation. Base oil antioxidants such as Aromatic amines, hindered phenols, alkyl heterocyclic lubricant compounds, and aromatic sulfides have been identified as reliable lubricant oxidation resistant and replacement for ZDDP [4-8]. Moreover, nitrogen or sulfur heterocyclic lubricant additives have been reported elsewhere to be effective antioxidant lubricant additives and they do not contain Zinc and Phosphorus which often rendered exhaust pipe catalytic converter inactive thereby increasing environmental pollution [9-11].Therefore, there is an urgent need to sustain the momentum of pursuing very active, reliable and environmental friendly antioxidant lubricant additive.

In recent times, the rapid improvement of computer speed and programs has to lead to the development of in-silico studies. Computational in-silico simulations act as a boundary between microscopic level, time duration and the macroscopic universe of real wet experiment [11]. Quantitative Structure-Properties Relationship (QSPR) which is a theoretical in-silico study was developed to effectively predict and design active leading compounds. QSPR often relate the experimental chemical properties of a group of compounds with its molecular structures. In-silico study has recorded tremendous success in predicting and designing lead compounds with improved properties [12, 13]. Also, molecular dynamic (MD) simulation is another in-silico method that could predict accurately the dynamic interaction energies of any potent compounds in close contact between and crystal simulation coated surface [13]. In this research, efforts were geared towards designing new active antioxidant lubricant additives and to investigate their dynamic binding energies on Diamond Like-Carbon and steel crystal surfaces through QSPR and MD simulation approach.

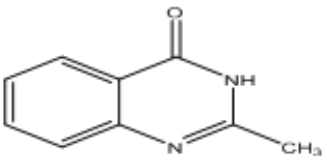
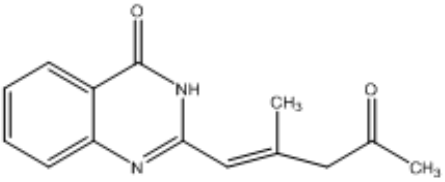
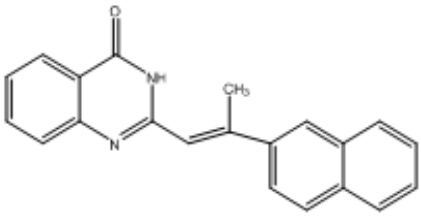
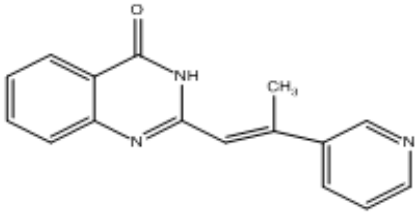
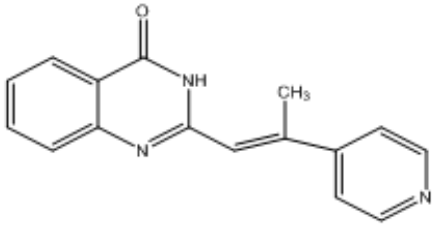
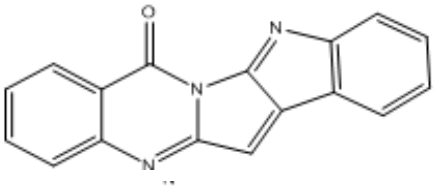
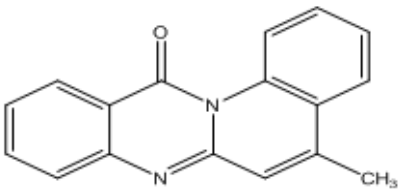
2. Materials and Methods

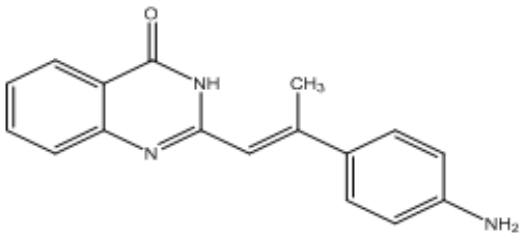
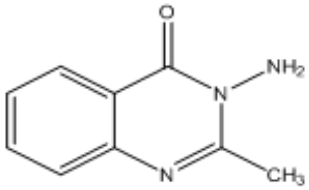
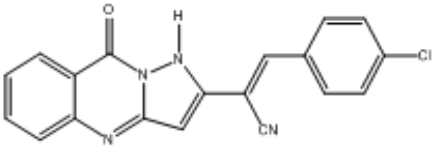
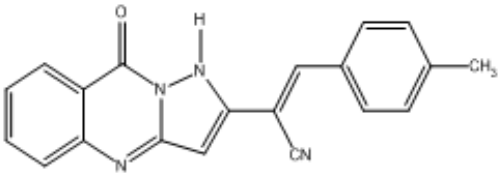
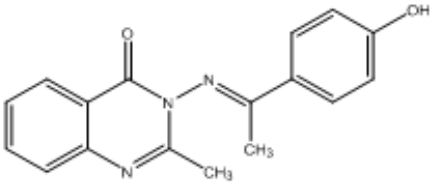
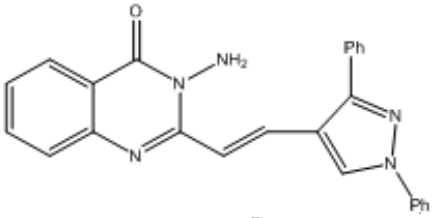
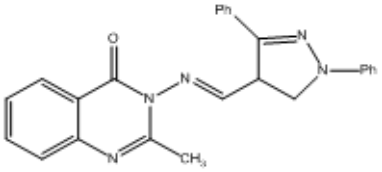
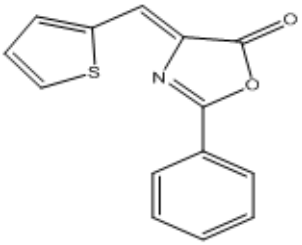
2.1 Data set, Molecular Descriptors Generation, QSPR model building and development

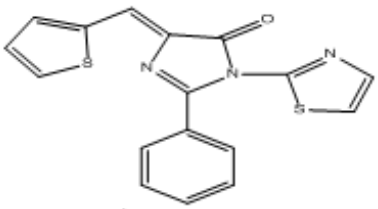
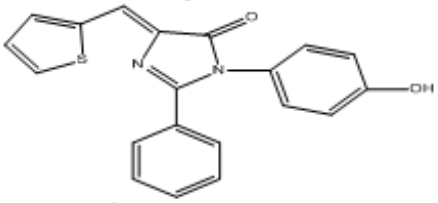
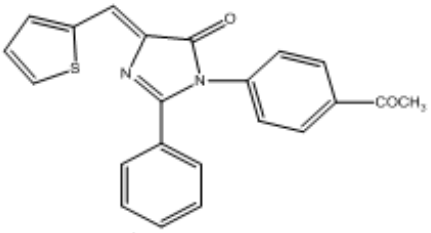
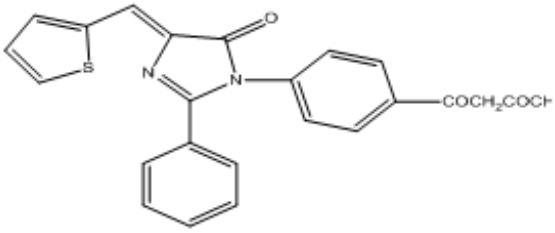
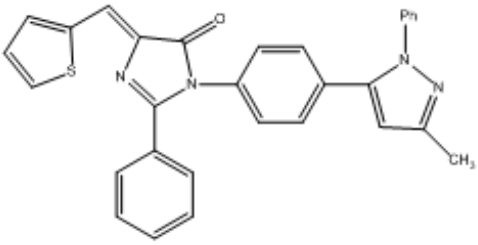
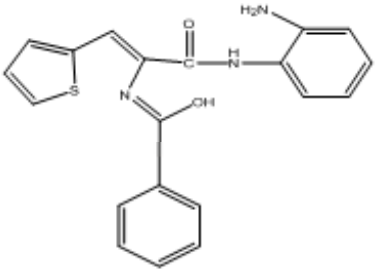
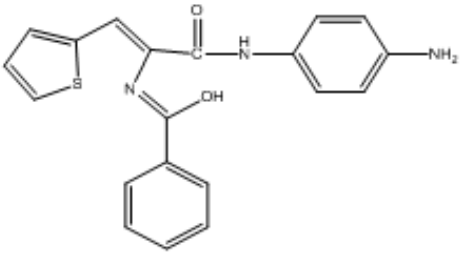
Some group of automobile engine data used for this investigation were made up of 37 (Table 1) compounds derived antioxidant lube oil additives obtained from the literature [14-16] with their antioxidant properties expressed in term of total acid values (0.1g/L), p(T.A.V 0.1g/L). All the selected heterocyclic derived 2D lubricant additives were completely optimized geometrically by Spartan'14 version 1.1.2 [17]. From the computational mathematical viewpoint, density functional theory (DFT/B3LYP/6-311++ G**) which can calculate excellent results compared to other in-silico methods [12, 13]. About 4234 molecular descriptors were jointly

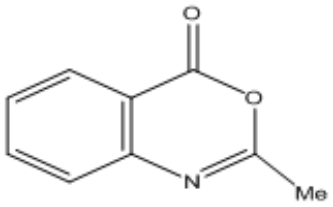
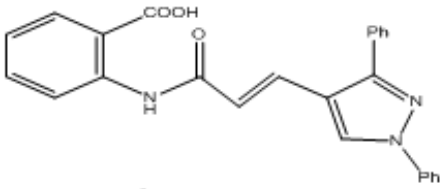
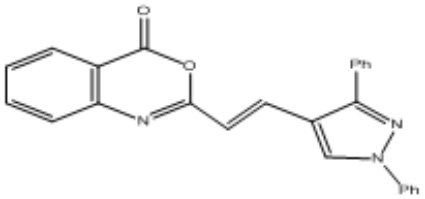
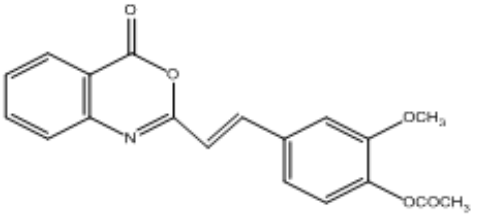
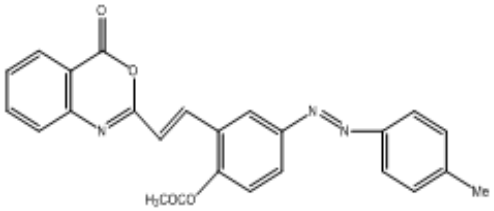
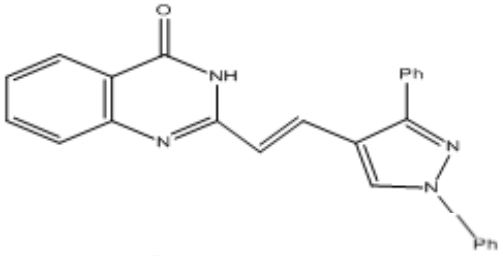
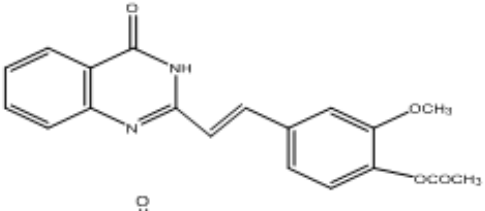
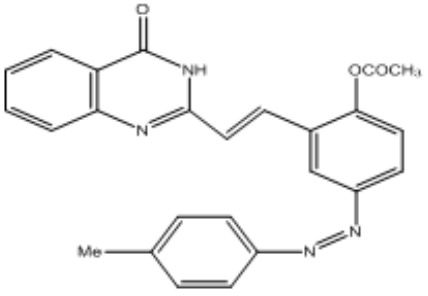
generated by Dragon 6.0 software toolkits and padel software [18] from the optimized base oil additives.

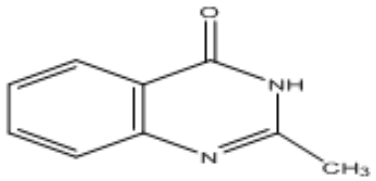
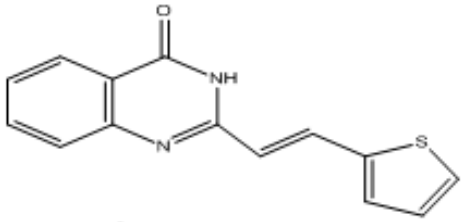
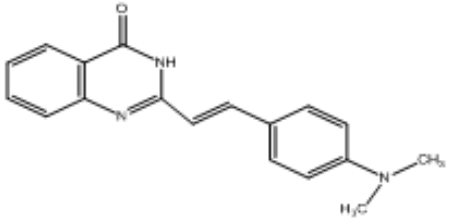
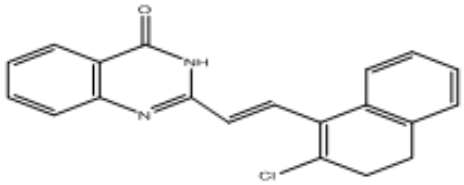
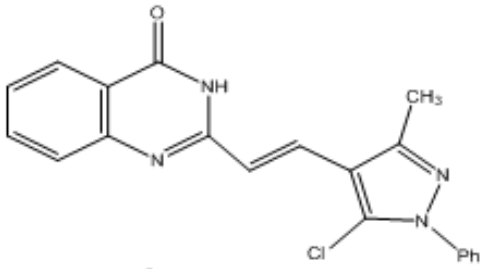
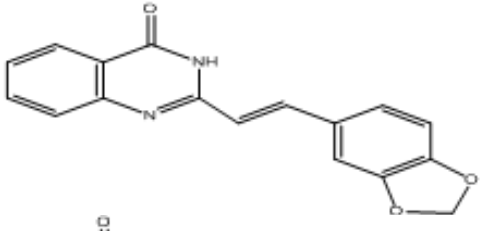
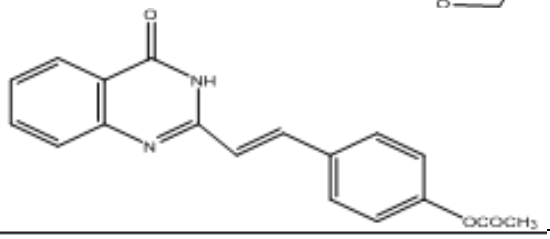
Table 1: Experimental, Predicted and Residual Antioxidant Lubricant Additive's Properties

S/N	2D Structures	Exp. A.L.A Properties (T.A.N.)	Predicted (TAV.0.1g/L)	Residual (TAV.0.1g/L)
01		10.19	9.88	0.31
02		6.80	6.70	0.10
03		7.66	6.78	0.88
04		7.28	7.49	7.28
05		7.61	7.49	-0.21
06		8.73	8.81	-0.08
07		8.79	8.70	0.09

08		8.82	7.82	1.00
09		10.41	10.34	0..07
10		6.05	6.90	-0.85
11		6.82	7.15	-0.33
12		5.32	8.88	-3.56
13		7.01	7.04	-0.03
14		7.70	8.30	0.40
15		5.10	5.10	0.00

16		4.8	4.91	-0.11
17		3.8	5.23	-1.43
18		5.5	5.44	0.06
19		2.73	2.69	0.04
20		1.5	1.50	0.00
21		2.57	4.41	-1.84
22		2.25	4.40	-2.15

23		10.74	9.60	1.14
24		10.64	8.56	2.08
25		9.07	7.48	1.59
26		9.64	9.70	-0.06
27		8.06	9.17	-1.11
28		7.57	7.77	-0.2
29		7.82	9.98	-2.16
30		6.16	9.45	-3.29

31		10.19	9.88	0.31
32		9.96	7.86	2.1
33		9.52	9.10	0.38
34		5.6	7.80	-2.2
35		9.63	8.52	1.11
36		6.55	7.99	-1.44
37		7.84	9.16	-1.32

A.L.A = Antioxidant Lubricant Additive, T.A.N= Total Acid Value.

Generated by Dragon 6.0 software toolkits and padel software [18] from the optimized base oil additives. Furthermore, the generated descriptors along with their experimental anti-friction properties were split into 65 per cent and 35 per cent by data division software. Using the 65% (24) data of the training sets, the genetic function algorithm (GFA) method in material studio chemical model building software version 8.0 was employed to perform the correlation analysis

between the anti-oxidant properties of the lubricant additives and the calculated molecular descriptors[12, 13]. The leftover 35% (13) were used to evaluate the reliability of the built QSPR models [19].

2.2*Assurance of the QSPR models and descriptors variance inflation factor (VIF) Determination*

The robustness and predictability of the constructed QSPR models were accessed by standard QSPR validation parameters [20] (Table 2). The squared correlation coefficient (R^2) (2.1) and the adjusted square correlation coefficient(R^2_{adj}) (2.2) and the Leave one out cross-validation coefficient (Q^2_{cv}) (2.3) are statistical values which must be greater than 0.5 but less than 1.0 for a robust and guaranteed QSPR model [20].

Table 2.0 Minimum recommended values of validated parameters for generally acceptable QSPR

Symbol	Name	Value
R^2	Coefficient of determination	≥ 0.6
$P_{(95\%)}$	Confidence interval at 95% confidence level	< 0.05
Q^2	Cross-validation coefficient	< 0.5
R^2_{ext}	Coefficient of determination for external test set	≥ 0.6
$R^2 - Q^2$	Difference between R^2 and Q^2	≤ 0.3
$N_{ext.\ test\ set}$	Minimum number of the external test set	≥ 5

$$R^2 = 1 - \frac{\sum(Yobserved - Ypredicted)^2}{\sum(Yobserved - Training)^2} \quad 2.1$$

$$R^2_{adj} = 1 - (1 - R^2)\frac{N-1}{N-P-1} = \frac{(N-1)R^2 - P}{N-P+1} \quad 2.2$$

$$Q^2 = 1 - \frac{\sum(Yp - Y)^2}{\sum(Y - Ym)^2} \quad 2.3$$

p = number of independent variables in the model, N = sample size [21],Yp = predicted property respectively, Y = observed property and $Y_{m\ =}$ mean property value of the training set [21]. The generated QSPR models were accessed externally with the aid of the value of R^2_{Pred} (3.4) [20].

$$R^2_{pred.} = 1 - \frac{\sum[Ypred(test) - Yobserved(test)]^2}{\sum[Yobserved(test) - Ymean(training)]^2} \quad 2.4$$

Moreover, the variance inflation factor (VIF) [22] was used to identifying the multicollinearity among variables. The VIF for the regression coefficient was expressed as:

$$\mathrm{VIF} = \frac{1}{(1-R^2)} \qquad 2.5$$

2.3 QSPR Model's Applicability domain (AD)

The AD of a QSPR model is characterized as a hypothetical area in compound space, characterized by the model descriptors and demonstrated reaction, and along these lines by the nature of the chemicals in the training set, as represented in each model by explicit sub-atomic descriptors. Therefore just the expectations for synthetic compounds falling inside this area can be viewed as solid and not demonstrate extrapolations [23]. The AD's leverage is a compound's distance space. The mathematics leverage (h_{ii}) of a compound of interest descriptor space can be calculated with the aid of equation. 2.6

$$h_{ii} = x_i^T (X^T X)^{-1} x_i \qquad 2.6$$

x_i= descriptor row matrix of the compound of interest, X= matrix carrying the structural information [24].

2.4 Template Based Lubricant Additives Design

A template-based chemical compound design technique was used to design new antioxidant lubricant additives with excellent properties. In the pool of experimental lubricant antioxidant additives, a template chemical compound with good leverage as well as excellent experimental properties was chosen as a useful scaffold toward the base for structural modification with the help of interpretations of molecular descriptors generated from the developed QSPR best model.

2.5 Study of dynamics molecular simulation

Dynamics molecular simulationstudy was performed out to access the designed compound's dynamic binding energy on the diamond-like carbon (DLC) crystal. The 3D structure of hydrogen-containing DLC crystal surface which was reported in many works of literature to be better allotropy of carbon in term of wearing resistance ability and antioxidant in the sliding [25-30]was constructed from the carbon (C) model using Materials studio 8.0 simulation software. This was done by cleaving the carbon surface at point 1.1 .0 (h k l), Top (1.006 Å) and Thickness (24.121 Å) into the crystal unit. Moreover, the repeated units (supercell) of the carbon crystal units were formed at U (9) and V (8) while hydrogenation of the

supercell, vacuum slab and geometric optimization was performed. The 2D structures of the lubricant antioxidant additives were drawn with Chemdraw software and were then converted to 3D structures by materials studio version 8.0 simulations Program, then optimized and saved by the same software.

2.6 Molecular dynamics simulation energy calculations

COMPASS II (phase Optimized Molecular Potentials for Atomistic Simulation Studies II) which is a robust and well-developed force field (than COMPASS) that was derived based on the fitting ability against a wide range of synthetic organic and inorganic compounds [31] was selected in the Materials studio 8.0 Software. The dynamic simulation binding energy (B.E) calculations were carried out after introducing the optimized lubricant additive compound into the simulation vacuum slab of geometrically optimized hydrogen-containing DLC crystal (24.82 Å ×24.82 Å ×45.27 Å) surface at 350.15 K and over a range of inter-surface separations. The binding energy was calculated by using equation 2.7 [32].

$$\text{Molecular Dynamic Binding Energy} = E_{\text{total}} - (E_{\text{Lubricant Additive}} + E_{\text{DLC Surface}}) \quad 2.7$$

3. Results and Discussion

QSPR Model

Some QSPR models were developed from the investigation of the structure-properties relationship of 37 synthesized antioxidant lubricant additives. In a pool of some developed QSPR models, the best model with the best-squared correlation coefficient (R^2), adjusted squared correlation coefficient (R^2adj), Leave one out cross-validation coefficient (Q^2) and the external validation (R^2ext) of values 0.999477,0.998823, 0.995547and 0.645 respectively were recognized and chosen as the overall best model with the most predictive power [21]. This predictive model p(TAV.0.1g/L), that was expressed in term of antioxidant total acid values (TAV 0.1g/L) was further used to predict many properties of some designed antioxidant lubricant additives.

p(T.A.V 0.1g/L) = -0.402710730 * CrippenLogP - 0.899668648* nAtomLAC - 7.181018099 * MDEN-33 + 0.413688209*nRotBt + 4.465137586 * WT.eneg + 5.439709. R^2 of 0.999477, R^2adj of 0.998823, Q^2 of 0.995547 and R^2_{ext} of 0.645.

Some QSPR statistical analyses were also carried out to further validate the identified model; the plot of experimental properties versus residual activities (Figure 1) indicated that there was no systemic error in the developed model as the propagation on both sides of zero in the graph was observed [32]. The plotted graph in figure 2 is in great concurrence with the

validation parameters [21] in table 2, and hence the developed model did not demonstrate any relative forms of error since the R^2 from the graph was found to be 0.7244.

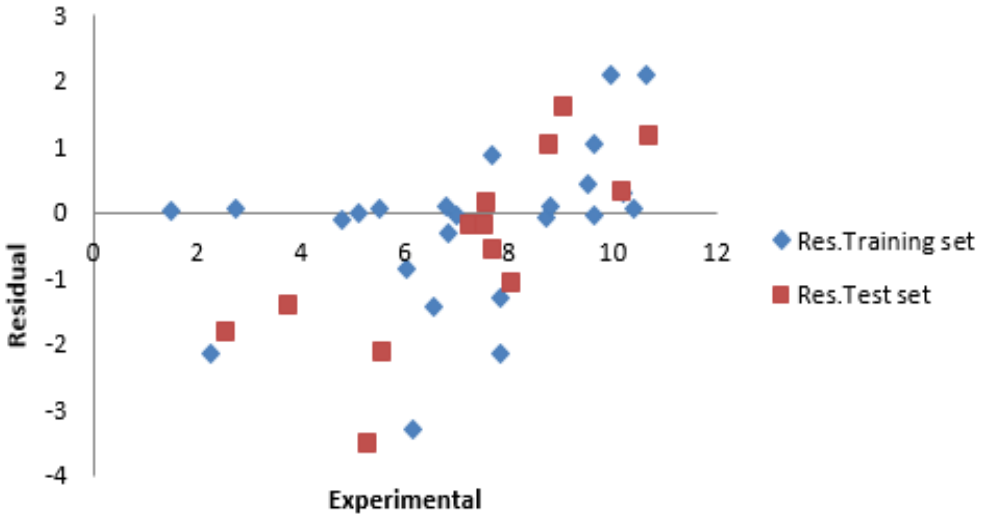


Figure 1: Residual against the experimental 0.01g/L values for the training and test sets of antioxidant lubricant additives

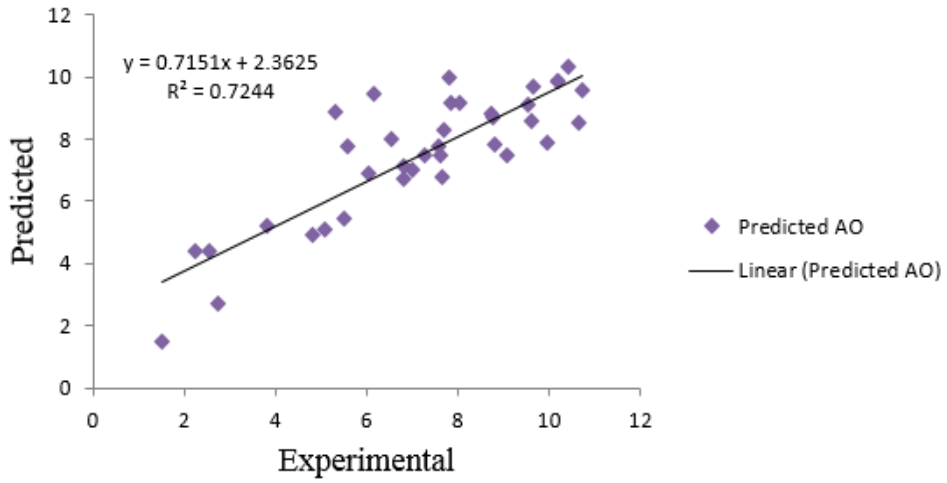


Figure 2: Residual against the experimental values for antioxidant lubricant additives

The QSPR model revealed that decrease in molecular descriptors such as CrippenLogP (Lipophilicity parameter/ character), nAtomLAC (Longest Aliphatic Chain Descriptor), MDEN-33 (Molecular distance edge between all primary carbons) and increase in nRotBt (Rotatable Bonds Count Descriptor) and WT.eneg (Non-directional WHIM, weighted by Mulliken atomic electronegativities) values will increase the antioxidant properties of the lubricant additive [18, 34].

3.2 Applicability domain's assessment of the developed model and molecular designs

To select the additive to use as a design template for further structural modifications since the robustness of the QSPR model alone cannot be enough to predict accurately the properties of all the compounds within the chemical space [35]. In Figure 3, William's plot which is the applicability domain's leverage plot was calculated and found to contain leverage danger, h* of 0.75.

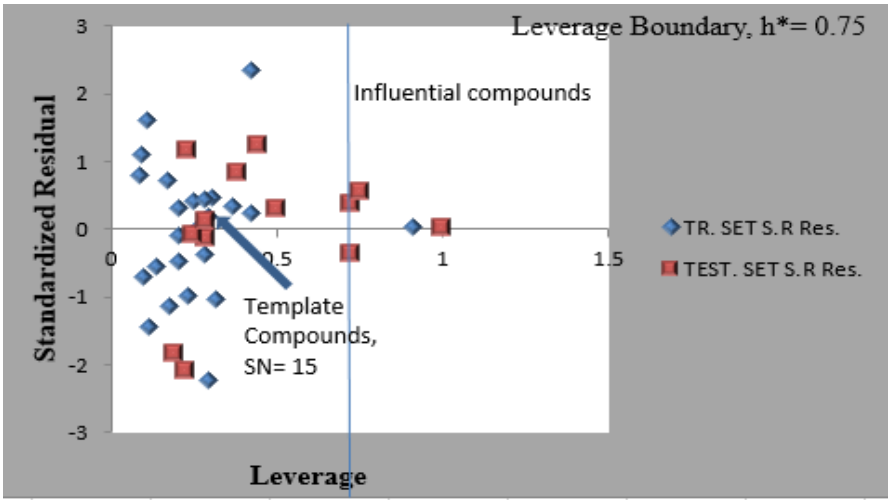


Figure 3: Williams plot for QSPR Model

This plot revealed that about five compounds (14, 20, 27, 17 and 21) that go beyond the leverage danger were termed as influential antioxidant lubricant additives [24]. These influential antioxidant lubricant additives are compounds that go beyond the danger leverage lines/chemical space and therefore, such compound cannot be used as design template [24]. The compound with serial number 15 (Table 1) has zero (0.00) residual value and was statistically observed to be inside the chemical space of William's plot with an excellent leverage value (Fig. 3) was chosen as the best template after which further modification was made.

From the developed QSPR model, the molecular descriptor with the highest/ contributor to the development of the model was WT.eneg (Non-directional WHIM, weighted by Mulliken atomic electronegativities). This descriptor was chosen as the best contributor due to the highest coefficient value among the co-descriptors. Therefore, interpretation of this descriptor revealed that addition of more weighted electronegative compound such as nitrogen atoms from NH_2 and other substituents like phenyl and methyl to the additive template (Fig. 4) revealed that better novel antioxidant lubricant additives were designed (Table 3). Moreover, all the five designed antioxidant lubricant additives along with their properties (total acid values) were found to be excellently better than the experimental antioxidant lubricant additives (Table 1).

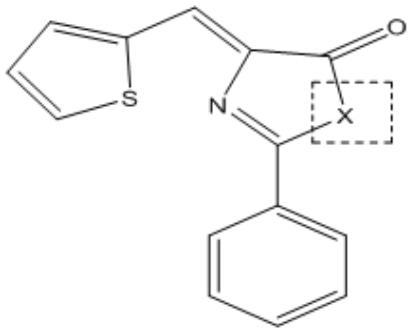
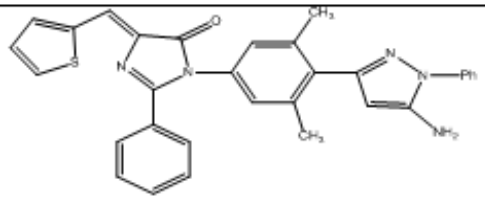
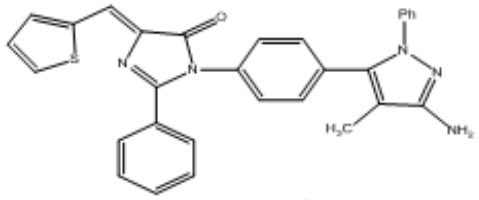
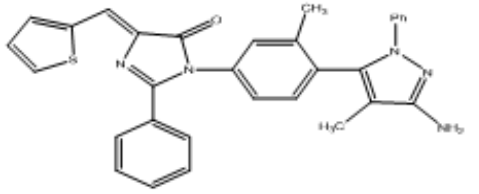
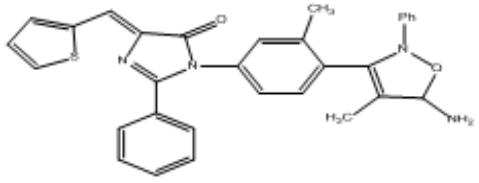
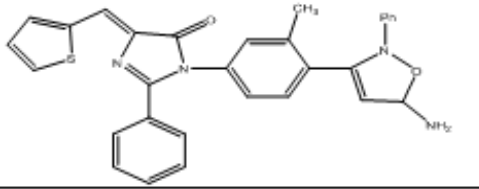


Figure 4: 2D Structural fragment of the chosen additive template.

Table 3: Novel Antioxidant Lubricant Additive's Properties and Dynamic Binding Energies

S/N	2D of Designed Compound	A.L.A Properties (T.A.N.)	Dynamic Binding Energy (kcal/mol)	
			Steel- A.L.A Complex	DLC-A.L.A Complex
1		0.850281	-171817	-12285.2
2		1.300557	172835	-12281.9
3		0.896965	-171767	-12278.8
4		1.144883	-171835	-12286.8
5		1.291393	-172870	-12286.4

A.L.A = Antioxidant Lubricant Additive, A.V= Acid Value, T.A.N= Total Acid Value, DLC = Diamond Like Carbon

3.3 Dynamic simulations assessment

The five designed antioxidant lubricant additives table 3 was revealed to be dynamically bound to the DLC and steel crystal surfaces excellently. Moreover, it can be observed that all the designed additives were found to dynamically bind to steel crystal surface better when compared to the DLC crystal surface. This study also revealed that (Z)-3-(4-(5-amino-2-phenyl-2,5-dihydroisoxazol-3-yl)-3-methylphenyl)-2-phenyl-5-(thiophen-2-ylmethylene)-3,5-dihydro-4H-imidazol-4-one with serial number 5 from table 3 was excellently bound to steel surface (-172870 kcal/mol) than its co-additives, while (Z)-3-(4-(5-amino-4-methyl-2-phenyl-2,5-dihydroisoxazol-3-yl)-3-methylphenyl)-2-phenyl-5-(thiophen-2-ylmethylene)-3,5-dihydro-4H-imidazol-4-one with serial number 4 was also excellently bound to DLC surface (-12286.8 kcal/mol) than other antioxidant lubricant additives (Table 3). Moreover, their dynamic binding energies and interaction complex were shown in figure 5.

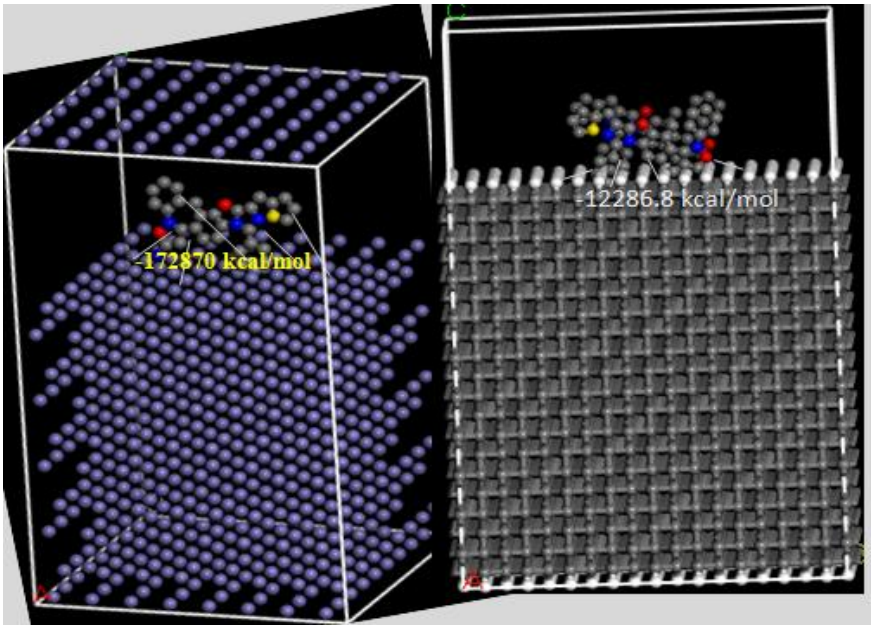


Figure 5: 3D of Fe-Ligand Complex (-172870 kcal/mol) and DLC-Ligand Complex (-12286.8 kcal/mol)

4. Conclusion

Quantitative structure-properties relationships (QSPR) which are an in-silico method was used to correlate 2D and 3D properties (descriptors) of antioxidant lubricant additives (compounds) with their properties. QSPR mathematical model along with molecular descriptors that have high coefficient value was used to design five new antioxidant lubricating base oil additives. All the novel additive's antioxidant properties were found to be better than the experimentally studied additives, with the novel lubricant additive (Z)-3-(4-(5-amino-1-phenyl-1H-pyrazole-3-yl)-3,5-dimethylphenyl)-2-phenyl-5-(thiophen-2-ylmethylene)-3,5-dihydro-4H-

imidazol-4-one found to possess excellent antioxidant properties of 0.850281 total acid values (T.A.V 0.1g/L). Moreover, this research revealed all designed additives were found to dynamically form better interaction to steel simulated coated surface than the DLC crystal simulated surface, and it was in agreement with our previous study [36]. The additives; (Z)-3-(4-(5-amino-2-phenyl-2,5-dihydroisoxazol-3-yl)-3-methylphenyl)-2-phenyl-5-(thiophen-2-ylmethylene)-3,5-dihydro-4H-imidazol-4-one and (Z)-3-(4-(5-amino-4-methyl-2-phenyl-2,5-dihydroisoxazol-3-yl)-3-methylphenyl)-2-phenyl-5-(thiophen-2 ylmethylene)-3,5-dihydro-4H-imidazol-4-one were revealed to be exceptionally bound to steel (-172870 kcal/mol) and to DLC (-12286.8 kcal/mol) crystal simulated surfaces than their co-additives . All the designed additives do not contain Phosphorus and Zinc which often rendered exhaust pipe catalytic converter inactive thereby increasing environmental pollution [9-11]. Moreover, from our dynamic simulation study, all the designed additives were found to dynamically bind to the simulated surface of steel than to DLC crystal simulated surface. This research has provided a theoretical framework towards synthesizing new and better antioxidant lubricating base oil additives that could hinder the base oil from undergoing a complete circle of oxidation.

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