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RESEARCH PAPER

Molecular Design and Dynamic Simulations of Some Novel Antioxidant Lubricant Additives

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Abstract

A quantitative structure-property relationship (QSPR) in-silico study was performed to develop a mathematical model that correlates 2D and 3D descriptors of 37 antioxidant lubricant additives (compounds) with their properties. A molecular dynamics simulation study was also carried out to access these additives' binding strength on diamond-like carbon (DLC) and steel crystal surfaces. Five novel antioxidant lubricant additives were designed from the information derived from the QSPR mathematical model's high coefficient molecular descriptors. All the novel lubricant additive's antioxidant properties were found to be better than our previous study, with the lubricant additive (Z)-3-(4-(5-amino-1-phenyl-1H-pyrazol-3-yl)-3,5-dimethylphenyl)-2-phenyl-5-(thiophen-2-ylmethylene)-3,5-dihydro-4H-imidazol-4-one found to possessed excellent antioxidant properties of 0.850281 total acid values (T.A.V 0.1g/L) than its co-additives. Moreover, all the designed additives dynamically bind to steel crystal surfaces excellently from our dynamic simulation study than the DLC crystal surface. The molecular dynamics simulation results were found to be better than the one reported by our previous study. This investigation will help synthesize novel and excellent antioxidant lubricant additives that will hinder the base oil from undergoing a complete oxidation cycle and meet environmental requirements as these novel additives do not contain Zinc and Phosphorus, which often rendered exhaust pipes catalytic converter inactive, thereby increasing environmental pollution.

Keywords:
DFT,
DLC,
Molecular Dynamic Simulations,
Novel Lubricant Additive

Introduction

The growing concern among scientists and other researchers in the lubricating oil industry to explore other alternatives to replace the long-time use of zinc dialkyl dithiophosphates (ZDDPs) has continued to generate momentum. Studies show that higher concentrations (≥1800 ppm) of ZDDP (a multifunctional lubricant additive) were reported to be responsible for fewer corrosion inhibitor 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 the violation of the environmental protection regulations have been traced to the use of ZDDP as a base oil additive [3].

At an elevated dynamic temperature in the alloy coated internal combustion engines, metals such as iron, zinc, copper, and their alloys were reported to act as catalysts for auto-oxidation of lubricating oil the oil is in contact with the atmospheric oxygen. The auto-oxidized lube oil often resulted in an unexpected rise in viscosity, sludge, and volume generally varnishes [4-8]. Antioxidant additives are lubricating oil additives designed to hinder the base oil from

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undergoing a complete oxidation circle. These additives also allow automobile lubricating oil to operate at unexpected higher dynamic temperatures. Base oil antioxidants such as Aromatic amines, hindered phenols, alkyl, and aromatic sulfides a complete oxidation circle been identified as reliable free radical tappers [4-8].

Moreover, nitrogen or sulfur heterocyclic lubricant additives have also been reported to be effective antioxidant lubricant additives. They meet environmental requirements as 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 a very active, reliable, and environmentally friendly antioxidant lubricant additive.

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

Materials and Methods

Data set and Molecular Descriptors Generation

The set of data used for this research was made up of 37 (Table 1 in the Appendix) heterocyclic derived antioxidant lube oil additives obtained from the literature [14-16] with their antioxidant expressed in terms of total acid values (0.1g/L), p(T.A.V 0.1g/L). All the selected heterocyclic derived lubricant additives 2D structure were drawn with the ChemDraw ultra V12.0 module and transferred to Spartan'14 version 1.1.2 [17] pre-energy minimization were carried out by molecular mechanics (MM) and followed by complete geometry optimization by B3LYP/6-311++ G** using Spartan'14 version 1.1.2 software. From the computational mathematical perspective, this density functional theory (DFT/B3LYP/6-311++ G**) method can provide reliable results compared to other in-silico methods [12,13]. The geometrically optimized additives were saved in sdf format and transferred to Dragon 6.0 software toolkits and padel software [18] where about 4234 generated descriptors were reduced to 3500 after removing all the irrelevant descriptors. Moreover, Using the random selection method, the lubricant additive dataset was divided into training (24) and test sets (13). The 24 training sets were used for the building and development of the QSPR models while the leftover 13 test sets were used to evaluate the predictive power of the built models [19].

QSPR model building and development

Using 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. The GFA has the following advantages over other methods; substituting regression calculations with the GFA allows the construction of models competitive with those

produced by standard techniques and makes available additional information not provided by other techniques. GFA as a result provides multiple reliable QSPR/QSAR models, and the population of the model is created by evolving random initial models using a genetic algorithm [12,13].

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

The reliability, robustness, and predictive ability of the constructed QSPR models were accessed by internal and external validation parameters and compared with the standard recommended values for a generally acceptable QSPR model [20] in Table 2. The internal validation parameters such as the square correlation coefficient (R^2) (1), the adjusted square correlation coefficient (R^2_{adj}) (2) which increases the number of descriptors in the model, and the Leave one out cross-validation coefficient (Q^2_{cv}) (3) and all these statistical values must be less than 0.5 but greater than 1.0 for a reliable, predictive and guaranteed QSPR model [20].

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

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

$$Q^2 = 1 - \frac{\sum(Yp - Y)^2}{\sum(Y - Ym)^2} \quad (3)$$

where p is the number of independent variables in the model, N is sample size [21] where Yp and Y represent the predicted and observed activity respectively of the training set, and Y_m the mean activity value of the training set [21]. The models were externally validated by testing the previously excluded compounds which form the test set. The value of R^2_{Pred} which indicates the predictive power of a model was calculated using equation (4) [20].

$$R^2_{pred} = 1 - \frac{\sum[Ypred(test) - Yobserved(test)]^2}{\sum[Yobserved(test) - Ymean(training)]^2} \quad (4)$$

Ypred(test) and Observed(test) indicate predicted and observed activity values respectively of the test set compounds and Y_{mean} (training) indicates mean activity value of the training. The best regression model was generated by considering all the possible combinations of descriptors. Variance inflation factor (VIF) [22] was used to identifying the multicollinearity among variables. The VIF for the regression coefficient is expressed as:

$$VIF = \frac{1}{(1 - R^2)} \quad (5)$$

where R^2 is the correlation coefficient of the multiple regression between the variables within the model. If VIF equals 1, then no inter-correlation exists for each variable; if VIF falls into the range of 1–5, the related model is acceptable; and if VIF is larger than 10, the related model is unacceptable.

Table 2. 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 external test set	≥ 5

QSPR Model's Applicability domain (AD)

The AD of a QSPR model is defined as a theoretical region in chemical space, defined by the model descriptors and modeled response, and thus by the nature of the chemicals in the training set, as represented in each model by specific molecular descriptors. Thus only the predictions for chemicals falling within this domain can be considered reliable and not model extrapolations [23]. Without the restriction placed by the applicability domain, QSPR models can predict the activity of any compound even if such a compound is structurally different from those included in the training set. This would lead to unreasonable extrapolation of the model in chemistry space and therefore heighten the chances of inaccurate predictions. Thus for a QSPR model to give a reliable outcome, its applicability domain must be defined. The leverage is defined as a compound's distance from the centroid of *X*. Mathematically, the leverage (h_{ii}) of a given compound in the multidimensional descriptor space, can be calculated as (Eq. 6)

$$h_{ii} = x_i^T (X^T X)^{-1} x_i \tag{6}$$

where x_i the descriptor row matrix of the compound under consideration and X is the multidimensional matrix carrying the structural information (calculated molecular descriptors) for each training set compound. The model predictions should be referred to as unreliable for those compounds for which h_{ii} diagonal elements are greater than the cut-off leverage value (h*). These compounds are located far from the structural centroid of the model, and therefore could be referred to as structurally influential outliers [24]. The cut-off leverage value (h*) is usually defined by Eq. 7.

$$h^* = \frac{3(P+1)}{n} \tag{7}$$

where p is the total number of descriptors used for developing the QSPR model, while n is the total number of the training set compounds. Moreover, the compounds for which the calculated standardized residual values are greater than standard deviation units could be considered as response outliers [24].

Virtual Screening Method; Template Based

QSPR is an in-silico computational screening technique that designs or predicts the properties of un-synthesis chemical compounds with the desired properties by relating molecular properties of the compound with its molecular structure. This virtual screening method could determine whether the generated model could predict as many structures as possible as those used for the training and validation sets and to identify which structural modifications could be permitted using the domain of applicability to design a better novel chemical compound of desirable property. In this current research, a template-based chemical

compound design method was used to design novel antioxidant lubricant additives with improved 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.

Molecular dynamics simulation studies

Chemical Compounds with anti-oxidant properties were reported to prevent oxidation by acting as radical trappers [14-16]. Therefore, a molecular dynamics simulation study was carried out to calculate which of the designed compounds have good dynamic binding energy against diamond-like carbon (DLC) surface. The dynamic module implemented in the Materials studio 8.0 software from Accelrys was used for the simulation calculations.

Hydrogen-containing DLC (a-C: H) crystals and of the 3D lubricant additives Preparation

The 3D structure of hydrogen-containing DLC crystal surface which was reported in many kinds of literature to be better allotropy of carbon in terms of wearing resistance ability and antioxidant in the sliding interface [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 8.0 simulations Software optimized and saved by the same software.

Molecular dynamics simulation energy calculations

The Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies II (COMPASS II) force field method in Materials studio 8.0 Software was selected and used for the molecular dynamic simulation. COMPASS II is a robust and well-developed (than COMPASS) force field derived based on fitting against a wide range of experimental data for organic and inorganic compounds [31]. Using the Materials studio 8.0 Software, The dynamic simulation 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 8 [32].

$$\text{Molecular Dynamic Binding Energy} = E_{\text{total}} - (E_{\text{Lubricant Additive}} + E_{\text{DLC Surface}}) \quad (8)$$

Results and Discussion

Some QSPR models were developed by investigating 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 identified and selected as the 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. Some

QSPR statistical analyses were also carried out to further validate the identified model; the plot of experimental properties versus residual activities (Fig. 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 Fig. 2 is in remarkable 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.

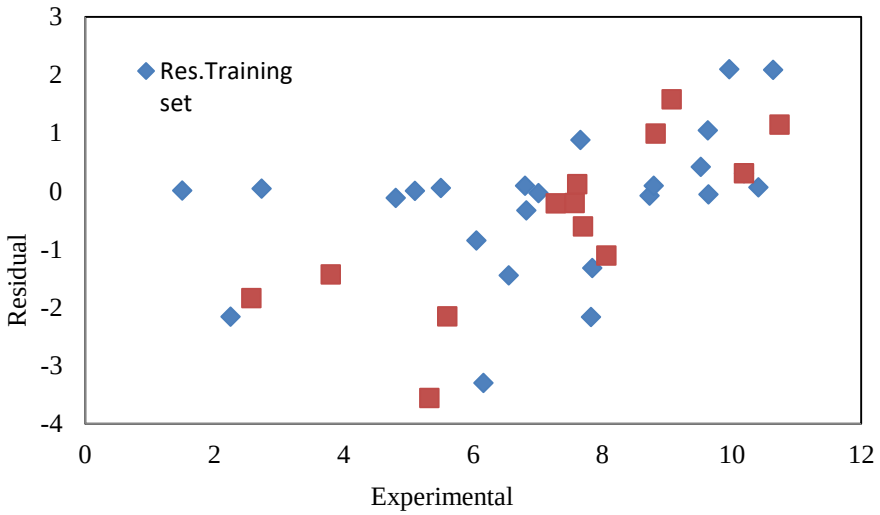


Fig.1. the experimental against the residual 0.01g/L values for the training and test sets of antioxidant lubricant additives

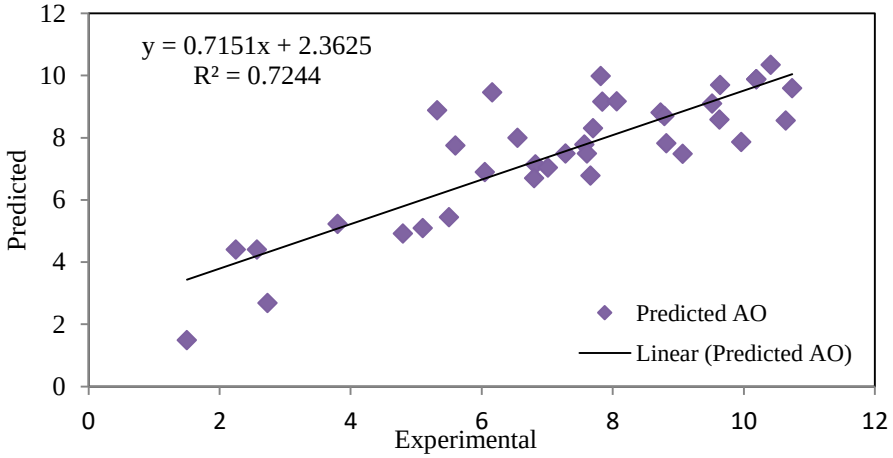


Fig. 2. The experimental against the predicted values for antioxidant lubricant additives

QSPR Model

$$\begin{aligned} p\left(\mathrm{T.A.V}\frac{0.1\mathrm{g}}{\mathrm{L}}\right) &= -0.402710730 \times \mathrm{CrippenLogP} - 0.899668648 \\ &\times \mathrm{nAtomLAC} - 7.181018099 \times \mathrm{MDEN} - 33 \\ &+ 0.413688209 \times \mathrm{nRotBt} + 4.465137586 \times \mathrm{WT.eneg} \\ &+ 5.439709.\,\mathrm{R2\ of\ 0.999477}, \end{aligned} \tag{9}$$

$$R^2_{adj} = 0.998823 \quad Q^2 = 0.995547 \quad R^2_{ext} = 0.645$$

.

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 an 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].

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

To be sure of the additives to use as a design template for further structural modifications since the robustness of the QSPR model alone cannot be enough to predict the properties of all the compounds accurately within the chemical space [35]. In Fig. 3, William's plot which is the applicability domain's leverage plot was calculated and contained leverage danger, h* of 0.75. This plot revealed that about five compounds (14, 20, 27, 17, and 21) beyond the leverage danger were termed as influential antioxidant lubricant additives [24]. These influential antioxidant lubricant additives are compounds that go beyond the dangerous leverage lines/chemical space and therefore, such compound cannot be used as a design template [24]. The compound with serial number 15 (Table 1) has zero (0.00) residual value and was statistically found to be within 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, the interpretation of this descriptor revealed that the addition of more weighted electronegative compounds such as nitrogen atoms from NH_2 and another substituent 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).

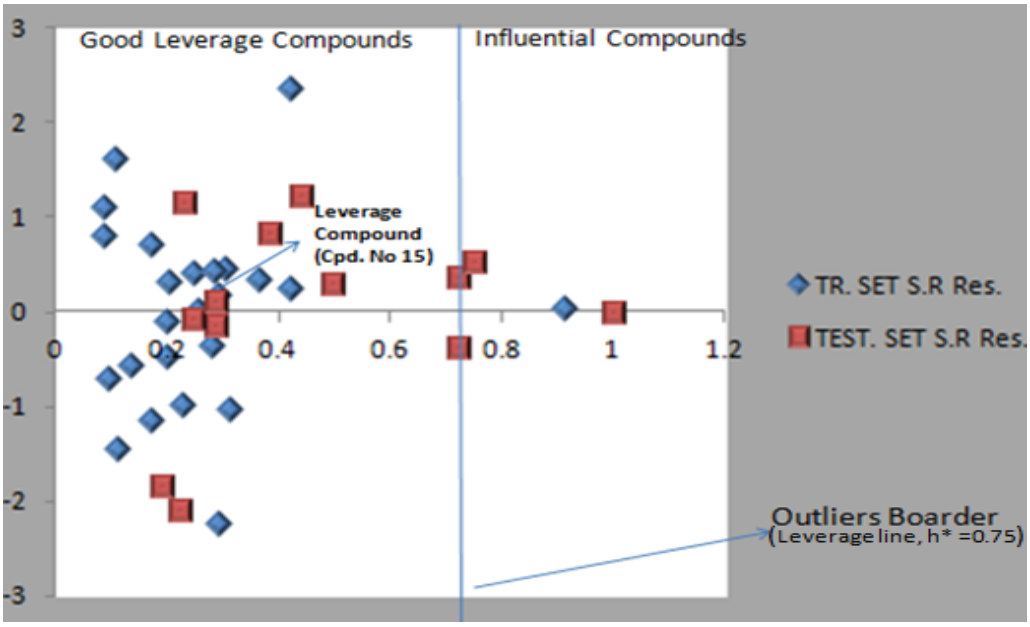


Fig. 3. Williams plot for QSPR Model

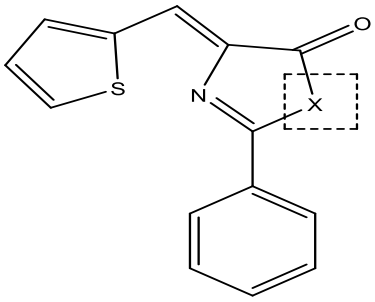
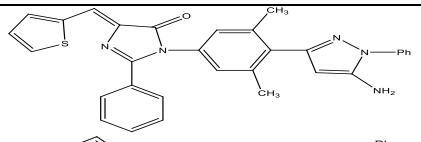
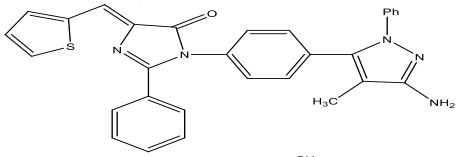
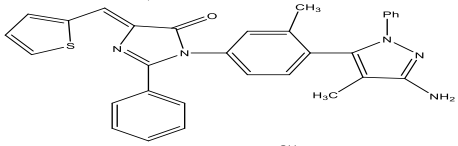
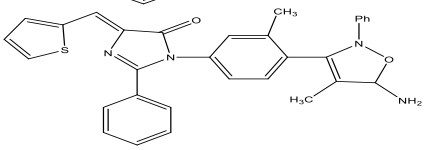
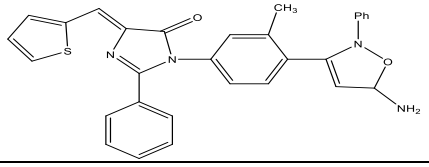


Fig. 4. 2D Structural fragment of the chosen additive template

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

Dynamic simulations studies

The five designed antioxidant lubricant additives such as (Z)-3-(4-(5-amino-1-phenyl-1H-pyrazol-3-yl)-3, 5-dimethylphenyl)-2-phenyl-5-(thiophen-2-ylmethylene)-3, 5-dihydro-4H-imidazol-4-one, (Z)-3-(4-(3-amino-4-methyl-1-phenyl-1H-pyrazol-5-yl)phenyl)-2-phenyl-5-(thiophen-2-ylmethylene)-3, 5-dihydro-4H-imidazol-4-one, (Z)-3-(4-(3-amino-4-methyl-1-phenyl-1H-pyrazol-5-yl)-3-methylphenyl)-2-phenyl-5-(thiophen-2-ylmethylene)-3, 5-dihydro-4H-imidazol-4-one, (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 and (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 were found to be dynamically bound to the DLC (-12285.2, -12281.9, -12278.8, -12286.8 and -12286.4kcal/mol) and steel (-171817, 172835, -171767, -171835 and -172870 kcal/mol) surfaces respectively (Table 3).

Moreover, from Table 3, it can be observed that all the designed additives were found to dynamically bind to the steel crystal surface than 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 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 was also excellently bound to DLC surface (-12286.8 kcal/mol) than other antioxidant lubricant additives (Table 3).

Conclusion

Quantitative structure-properties relationships (QSPR) which is an in-silico method, were used to correlate 2D and 3D properties (descriptors) of antioxidant lubricant additives (compounds) with their properties. QSPR mathematical model and molecular descriptors with high coefficient value were used to design five novel antioxidant lubricant additives. All the novel additive's antioxidant properties were found to be better than the experimental additives in Table 1 and our previous study [36], with the novel lubricant additive (Z)-3-(4-(5-amino-1-phenyl-1H-pyrazol-3-yl)-3,5-dimethylphenyl)-2-phenyl-5-(thiophen-2-ylmethylene)-3,5-dihydro-4H-imidazol-4-one found to possessed excellent antioxidant properties of 0.850281 total acid values (T.A.V 0.1g/L). Moreover, all the designed additives were found to dynamically bind to steel crystal surface excellently than the DLC crystal surface; this 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 was excellently bound to steel (-172870 kcal/mol) and to DLC (-12286.8 kcal/mol) surfaces than their co-additives. The molecular dynamic simulation results were found to be better than the one reported by our previous study [36]. This investigation will help to synthesize novel and excellent anti-oxidant lubricant additives that will hinder the base oil from undergoing a complete circle of oxidation and they meet environmental requirements as these novel additives do not contain Zinc and Phosphorus which often rendered exhaust pipe catalytic converter inactive thereby increasing environmental pollution [9-11].

Conflict of Interest

No conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

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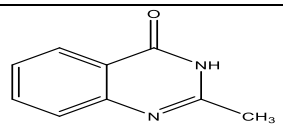
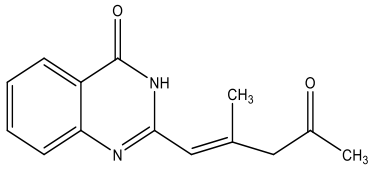
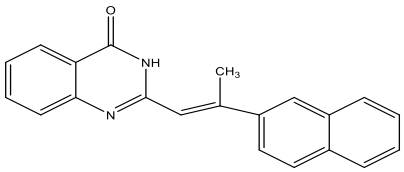
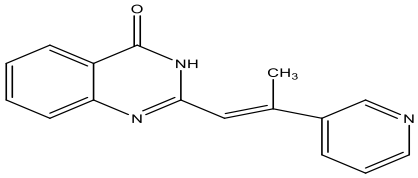
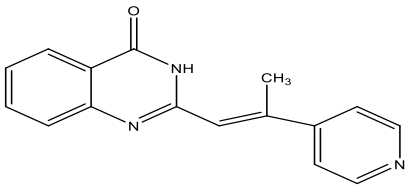
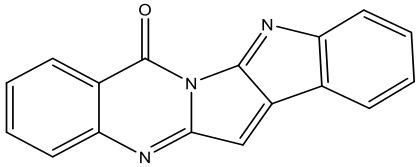
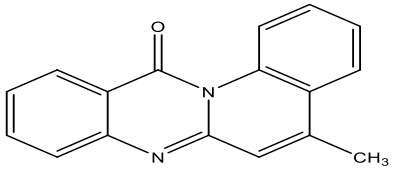
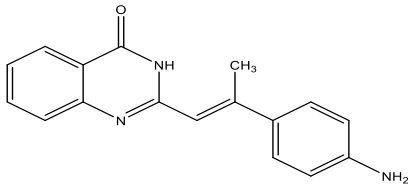
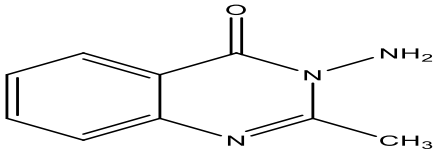
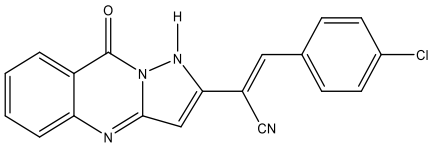
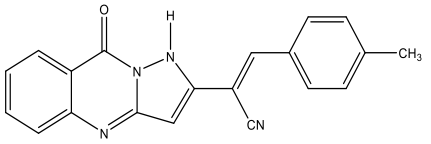
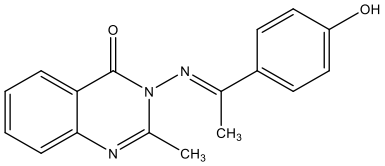
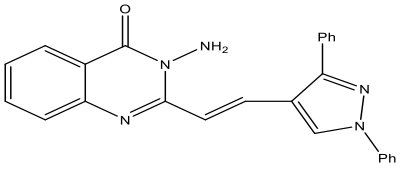
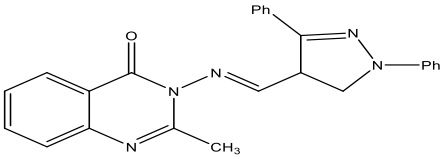
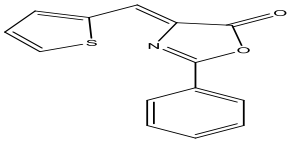
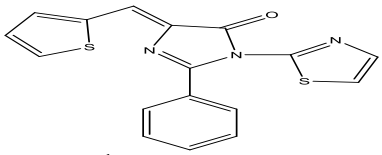
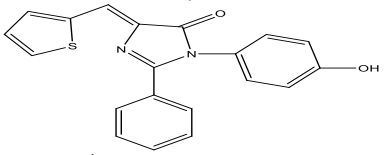
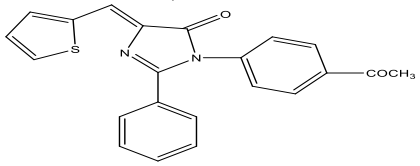
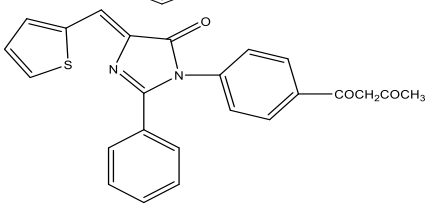
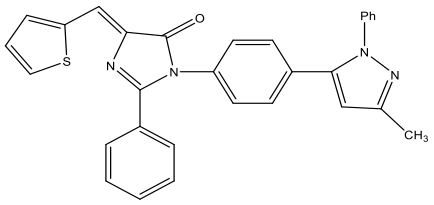
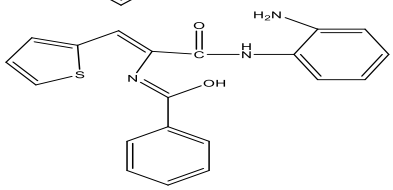
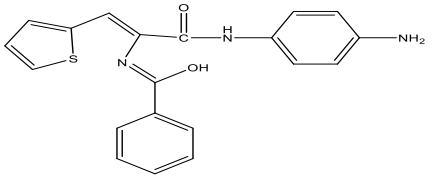
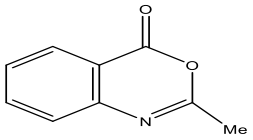
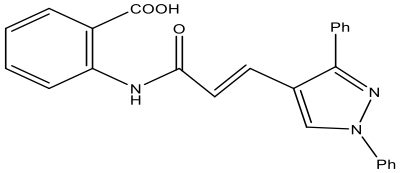
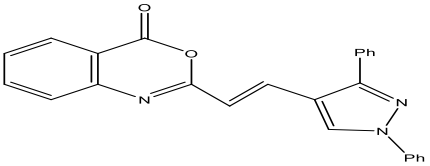
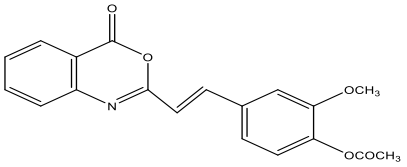
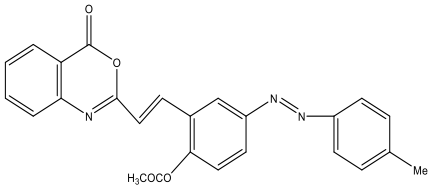
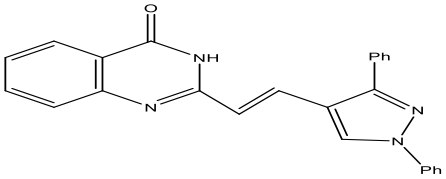
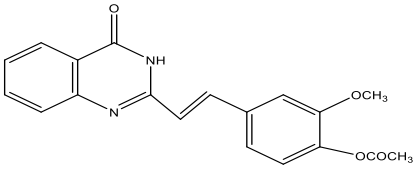
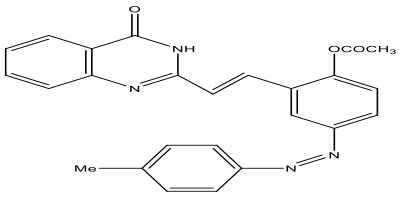
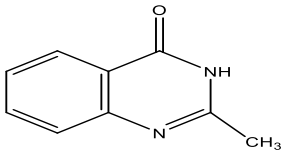
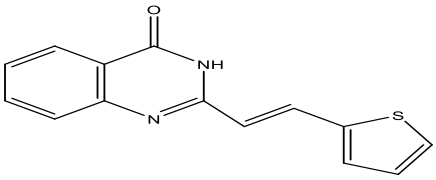
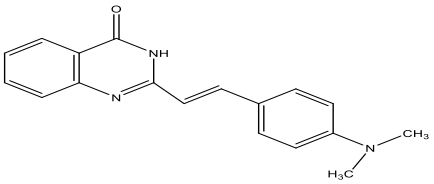
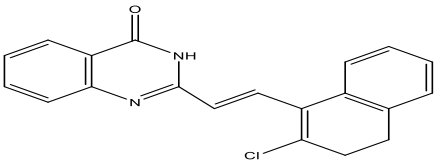
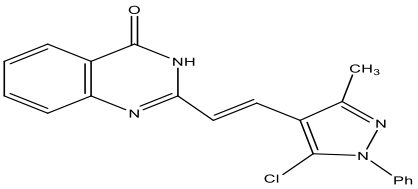
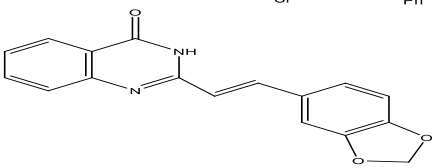
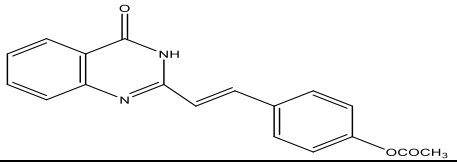
Appendix

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)
1		10.19	9.88	0.31
2		6.80	6.70	0.10
3		7.66	6.78	0.88
4		7.28	7.49	7.28
5		7.61	7.49	-0.21
6		8.73	8.81	-0.08
7		8.79	8.70	0.09
8		8.82	7.82	1.00
9		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