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PREPARATION AND EVALUATION OF SOME ANTIOXIDANT LUBE OIL ADDITIVES

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Abstract

In the present work, some antioxidants lube oil additives based on zinc dialkyl di thiophosphate were prepared by two steps, the first step is the reaction of different alcohols (n-butyl, isobutyl and mixture of isobutyl and amyl) with phosphorus pentasulphide to prepare O, O`- dialkyldithiophosphoric acid (DPDA), second step is the product dialkyldithiophosphoric acid (DPDA) was neutralized with zinc oxide. The structures of the prepared compounds were confirmed by Infra-Red Spectroscopy, Elemental Analysis and Determination of the molecular weights by using Gel Permeation Chromatography (GPC). All the prepared compounds were soluble in lube oil. The efficiency of the prepared compounds as antioxidants lube oil additives was investigated. It was found that the prepared compounds based on mixture of isobutyl and amyl alcohol give the best results as antioxidant lube oil additives. The Quantum mechanical parameters such as the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) energy levels, the energy gap (E_{HOMO}-E_{LUMO}) were calculated. The quantum chemical calculations were on the same line with the experimental results.

Keywords: Lube oil additives; antioxidant; zinc dialkyl dithiophosphate.

1. Introduction

One of the most important aspects of lubricating oils is the oxidation stability to be maximized. Exposure of hydrocarbons to oxygen and heat will accelerate the oxidation process. The internal combustion engine is an excellent chemical reactor for catalyzing the process of oxidation. Also, the engine's metal parts, such as copper and iron, act as effective oxidation catalysts. Thus, engine oils are probably more susceptible to oxidation than any other lubricant application [1]. Organic species in mineral oils and lubricants are subjected to deterioration by oxidation, especially at high temperatures and in the presence of air and metal. The lube oils suffer from auto-oxidation as a result of contact with air at elevated temperatures for long periods and in contact with metals, to form oxygenated compounds that increase the oil viscosity and motor metal corrosions [2]. Antioxidants are additives designed to prolong the life of a lubricant by increasing the oxidative resistance of the base oil. Antioxidants allow lubricants to operate at higher temperatures than would otherwise be possible without them. A number of such engine oil additives are known and employed in practice. Zinc dialkyldithiophosphates are, for example, because of their favorable characteristics as an antiwear agent and performance as oxidation inhibitor, contained in most all of the commercially available internal composition in motors [3]. Under boundary conditions, antioxidants film shears instead of surface material. One common anti-wear additive is zinc dialkyldithiophosphate ZDDP [4]. It reduces the risk of metal-to-metal contact, which can lead to increased heat, result in oxidation and negatively affect the film strength. Whether they are enhancing, suppressing or imparting new properties to the base oil, additives play an important role in the lubrication of machinery [5-6]. The ease of decomposition of the ZDDP correlates to the structure of the alkyl side chains, with additives derived from secondary alcohols being more effective than those from primary alcohols. The length of the side chain length only affects the antioxidant solubility, whilst the degree of branching has little overall effect [7]. ZDDP's retard bearing corrosion by two mechanisms, peroxide decomposition and the formation of a protective film. Secondary alkyl ZDDP's were found to be more effective corrosion inhibitors than primary alkyl ZDDP's because they were more easily decomposed [8-11]. In the present work we prepared some multifunctional lube oil additives based on zinc dialkyldithiophosphte and evaluated as antioxidant, detergent /dispersant for lube oil.

2. Experimental

Zinc dialkyldithiophosphte are synthesized in two steps. At the first step preparation of O, O`- dialkyldithiophosphoric acid (DPDA). Second step neutralization of (DPDA) with zinc compound

2.1. Preparation of O, O`- dialkyldithiophosphoric acid (DPDA)

O, O`- dialkyldithiophosphoric acid (DPDA) is synthesized by reaction of four moles of different alcohols (n-butyl, isobutyl and mixtur of isobutyl and amyl) with phosphorus pentasulphide:

1. In flask fitted with condenser, thermometer to control the temperature of the reaction and mechanical stirrer, 4 mole of alcohol was added and phosphorus pentasulphide added drop wise to the flask at temperature 50°C to about 70°C. After complete addition the temperature was maintained to 90 to 100°C for 3-5 hours with stirring
2. Separating the thio acid with nitrogen until the thio acid tests negative for H_2S with lead acetate paper
3. The distilled is removed and remaining mixture cooled and filtered to remove residual P_2S_5 and give product A, B and C.

2.2. Neutralization of dialkyldithiophosphoric acid (DPDA)

Second step: Under continuous stirring. The resulting O,O`dialkyldithiophosphoric acids (A, B and C) was neutralized with basically reacting zinc compound such as zinc oxide to give three compounds A_1, B_1 and C_1.

2.3. Analysis of products

2.3.1. IR spectroscopic analysis

IR spectra of the prepared esters were determined by using FTIR spectrometer Model Type Mattson Infinity Series Bench Top 961.

2.3.2. Elemental analysis

The percentage of S, C and H were determined in the prepared compounds by elemental analysis using CHNS-932 (LECO) Vario Elemental Analyzers. The percentage of Zn was determined in the prepared compounds by Graphite Furnence spectroscopy Analyticjena Zeenit 700 Germany. The percentage of P were determined in the prepared compounds quantitatively in weight by IP 148/58 method.

2.3.3. Determination of the molecular weights

The molecular weights of the prepared compound were determined by using gel permeation chromatography (GPC), Water 600 E.

2.4. Evaluation of the prepared compounds as lube oil additives

2.4.1. Evaluation as antioxidants:

The prepared compounds zinc dialkyldithiophosphate (A_1, B_1 and C_1) were added to the sample of SAE-30 in concentrations ranging from 0.25% to 1.5% and blends obtained were subjected to severe oxidation conditions using the Indiana Test Method, at 165.5°C with continuous rate of stirring. Samples were taken at intervals of 24 hours and up to 72 hours of oxidation and tested for their oxidation stability expressed as an increase in viscosity ratio

V/V_o and optical density Log I_o/I of the doped lubricating oil samples with respect to the undoped sample [12].

Variation of viscosity ratio V/Vo

The variation of viscosity ratio (V/Vo) was determined using IP 48/86 method, where V = Kinematic viscosity at 40 °C of sample after oxidation; V_o= Kinematic viscosity at 40 °C of sample before oxidation.

Change in total acid number (ΔTAN)

The change was calculated according to IP 177/83 method, where ΔTAN = total acid number of sample after oxidation – total acid number of sample before oxidation.

Optical density using IR technique

The IR spectra of oxidized oils have been determined in the range of the carbonyl group absorbance (1500-1900cm^{-1}) .The spectra have been superimposed upon that of the unoxidized oil. The absorbance (A) has been calculated according to: A= Log I_0/I, where I= % transmittance of the oil after oxidation; I_0 = % transmittance of the oil before oxidation [13-14].

Determination of sludge

10 gm of the test oil was taken in the centrifuge tubes for 1hr in the centrifuging operation (4233_{ECT} laboratory centrifuge) at 3000 rpm. After centrifuging, the clarified oil is decanted off, then 10 ml of isooctane is added as wash liquid to the tube containing the sludge in the form of a cake, and the sample is again centrifuged for 15min. the operation is repeated until the sludge is washed completely free of oil. The washed sludge, together with the centrifuge tube, is brought to weight in a thermostat at 105℃ and the amount of sludge is determined by weighing and expressed as a percentage of the original oil sample [15].

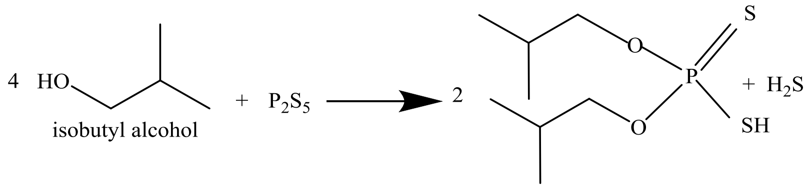
$$\%\ \text{Sludge} = \frac{\text{Weight of sample after centrifuge}}{\text{Weight of sample}} \times 100$$

Quantum mechanical program

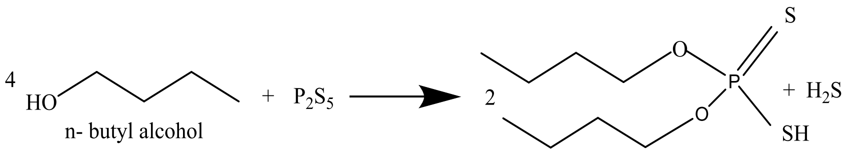
Chem bio drow ultra program was used for the molecular modeling and calulations. [16]

3. Results and discusion

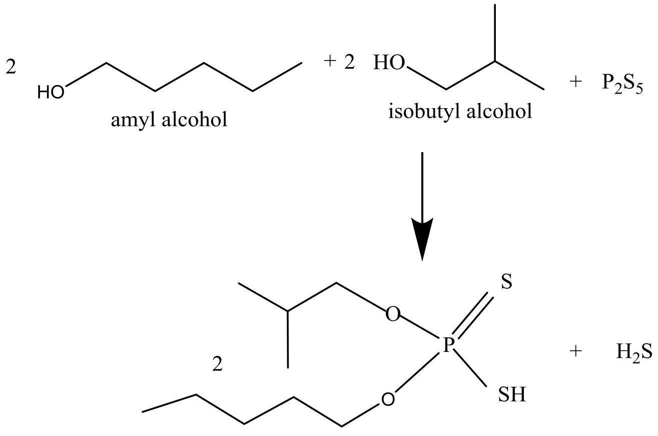
The dialkyl dithiophosphoric acid were prepared by using different alcohols (n-butyl, isobutyl and mixture of isobutyl and amyl) so we have three different products A, B and C.



O, O- di isobutyldithiophosphoric acid (B)



O, O- dibutyldithiophosphoric acid (A)



O, O- amylisobutyldithiophosphoric acid (C)

The IR spectrum of acids A, B and C are identical so that they illustrates the Figures (1-3).

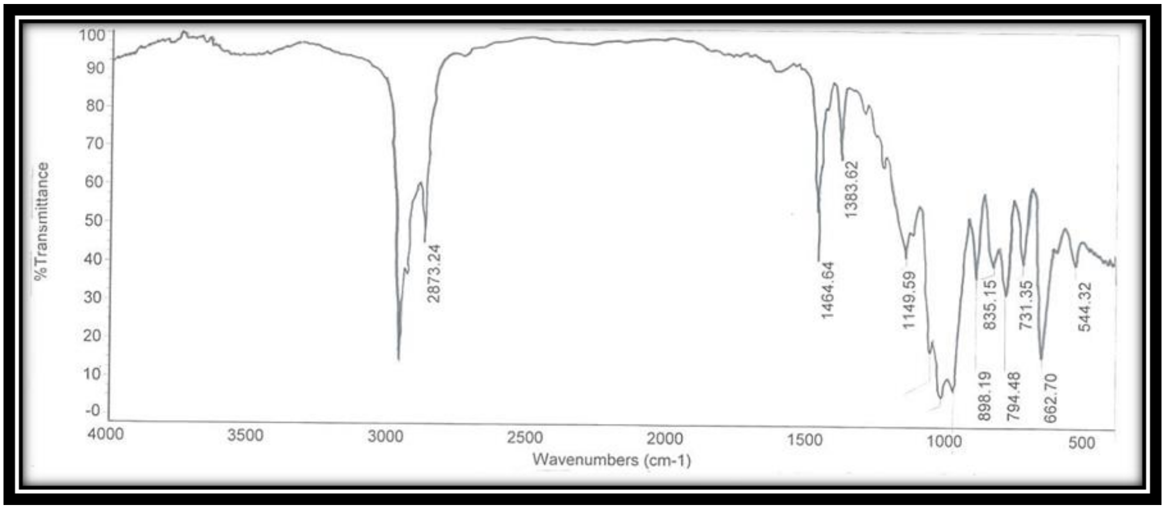


Fig. 1 Infrared structure of the prepared compound (A)

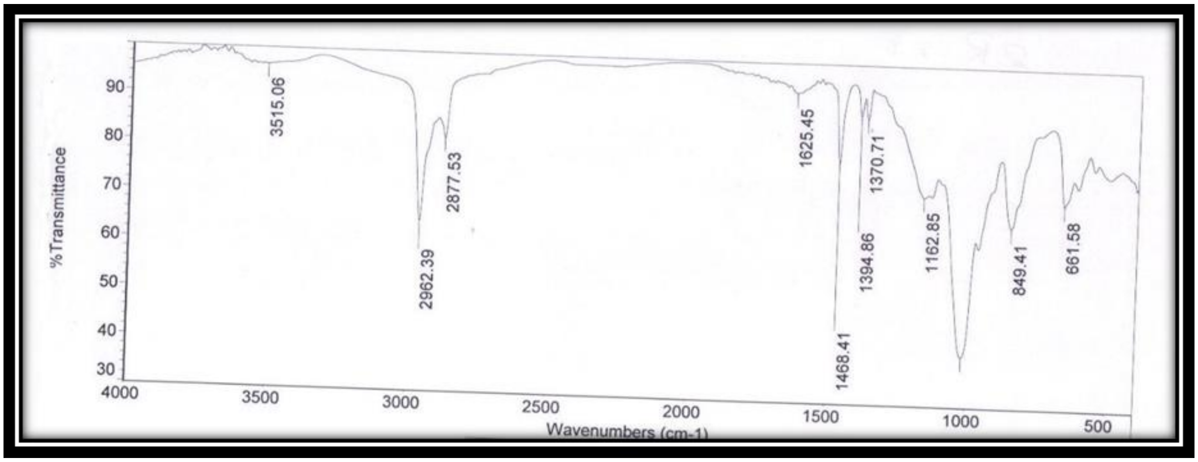


Fig. 2. Infrared structure of the prepared compound (B)

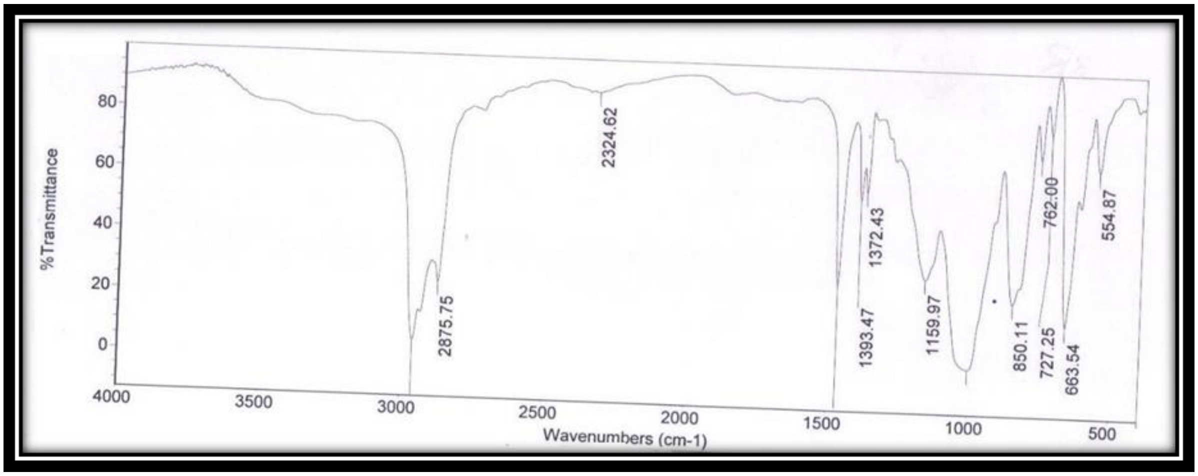
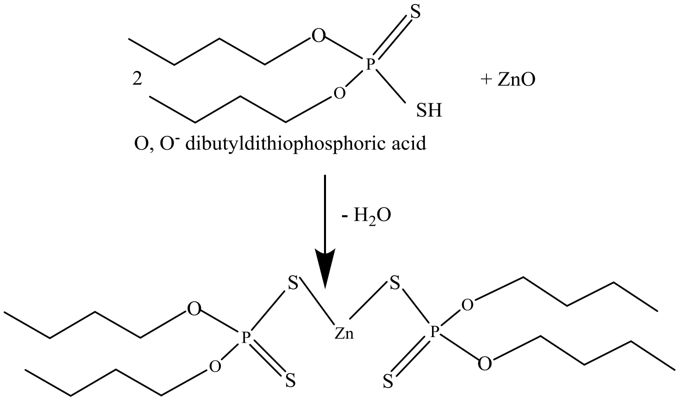


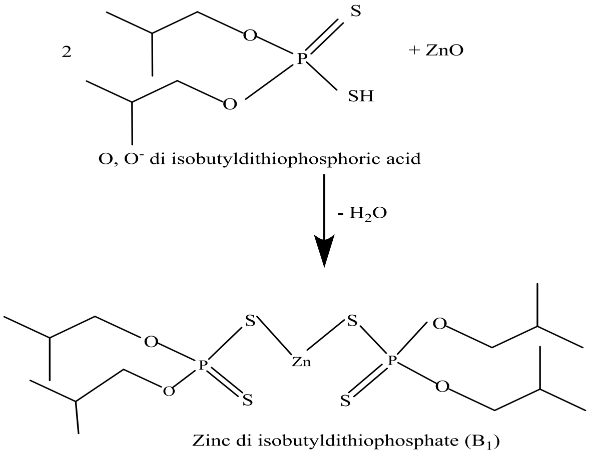
Fig. 3. Infrared structure of the prepared compound (C)

Disappearance of broad band at 3100-3400 cm^{-1} for OH of alcohols and presence of band P-S at 544.32, P=S band at 662.7 and band of C-O-P at 998 cm^{-1}.

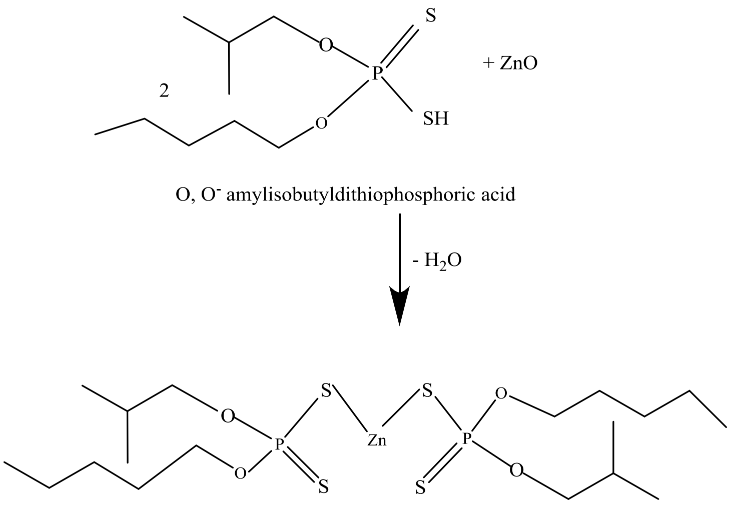
Then the prepared acids were neutralized with zinc oxide and then we obtain three different compounds (zinc dibutyldithiophosphate A_1, zinc di isobutyldithiophosphate B_1 and zinc amyl-isobutyldithiophosphate C_1).



Zinc dibutyldithiophosphate (A_1)



Zinc di isobutyldithiophosphate (B_1)



Zinc amylisobutyldithiophosphate (C_1)

The elemental analysis of the prepared zinc dialkyldithiophosphate (A_1, B_1 and C_1) were determined and given in Table (1), The percentage of Zn, S, C, P and H were determined

The molecular weight of the prepared compounds (A_1, B_1 and C_1) were determined and given in Table (2), it was found that they are very near to those calculated theoretically.

Table 1. Elemental analysis of the prepared compounds

Sample	Zinc%		S %		P%		C%		H%		O%	
	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
A_1	8.43	9.90	16.53	11.911	7.99	9.54	48.01	48.24	10.79	11.70	8.25	8.709
B_1	8.27	10.50	16.22	11.948	7.84	9.26	48.62	48.92	10.96	11.86	8.09	7.512
C_1	8.44	8.45	16.56	13.865	8	9.76	48.07	48.11	10.67	11.50	8.26	8.315

Table 2. Theoretical and determined mean molecular weights of the prepared compound (A_1, B_1 and C_1)

Prepared compound	Theoretical	Determined
A_1	547	550
B_1	547	545
C_1	603	605

3.1. Evaluation of the prepared compounds as lube oil antioxidants additives

The prepared compound A_1, B_1 and C_1 were added to the sample of SAE-30 in concentrations ranging from 0.25% to 1.5% and blends obtained were subjected to severe oxidation conditions using the Indiana Test Method, at 165.5°C with continuous rate of stirring. Samples were taken at intervals of 24 hours and up to 72 hours of oxidation and tested for their oxidation stability expressed as an increase in viscosity ratio V/V_o ,total acid number (ΔTAN), and optical density Log I_o/I of the doped lubricating oil samples with respect to the undoped sample. The variation ratios V/V_o with oxidation time for all doped samples are in Tables (3-11).

At any oxidation time the undoped oil always attained at higher values of V/V_o than those obtained from the oil samples blended with the prepared additives .in all cases, the results indicate that there is big difference between the lube samples mixed with prepared products and that of the neat lube oil. The efficiency of the prepared compound C_1 as an antioxidant is better than A_1 and B_1. The measured values of V/V_o for the doped oil samples with concentrations ranging between $0.25x\ 10^3$ ppm to $1.00\ x\ 10^3$ ppm are plotted in Table (3-11). These plots reveal that the maximum activity is attained when the concentration of the additives is $0.5\ x\ 10^3$ ppm. Further increase in additives concentration leads to a slight reduction in the activity of this additive. In this respect, it seems that when the concentration increases, the solubility of the prepared compound decreases. Accordingly, the dispersion of the additive in the lube oil decreases with increases in concentration. In all cases results indicate that there is a wide difference between the lube oil samples mixed with prepared products and those without additives.

Table 3. Variation of V/V_o with oxidation time of lube oil without and with prepared compound A_1

Sample	0	24	48	72
0.25%	1	1.308	1.718	2.27
0.5%	1	1.447	2.09	2.18
1%	1	1.3613	2.26	2.181
1.5%	1	1.307	2.335	2.08
Oil only	1	1.979	2.655	3.803

Table 4. Variation of ΔTAN with oxidation time of lube oil without and with prepared compound A_1

Sample	0	24	48	72
0.25%	0	1.6	2.16	3.72
0.5%	0	0.58	0.75	1.31
1%	0	0.81	1.13	2.36
1.5%	0	0.85	1.19	2.17
Oil only	0	1.63	4.12	10.52

Table 5. Variation of Log I_o/I with oxidation time of lube oil without and with prepared compound A_1

Sample	0	24	48	72
0.25%	0	0.09	0.102	0.25
0.5%	0	0.05	0.07	0.16
1%	0	0.091	0.109	0.27
1.5%	0	0.095	0.105	0.344
Oil only	0	0.0263	0.1165	0.3651

Table 6. Variation of V/V_o with oxidation time of lube oil without and with prepared compound B_1

Sample	0	24	48	72
0.25%	1	1.308	1.607	1.9
0.5%	1	1.064	1.096	1.096
1%	1	1.126	1.227	1.439
1.5%	1	1.00	1.098	1.354
Oil only	1	1.979	2.655	3.803

Table 7. Variation of ΔTAN with oxidation time of lube oil without and with prepared compound B_1

Sample	0	24	48	72
0.25%	0	1.7	2.15	3.52
0.5%	0	0.58	0.80	1.25
1%	0	0.80	1.13	2.34
1.5%	0	.85	1.23	2.01
Oil only	0	1.63	4.12	10.52

Table 8. Variation of Log Io/I with oxidation time of lube oil without and with prepared compound B_1

Sample	0	24	48	72
0.25%	0	0.09	0.103	0.19
0.5%	0	0.02	0.09	0.1
1%	0	0.08	0.110	0.21
1.5%	0	0.9	0.109	0.27
Oil only	0	0.0263	0.1165	0.3651

Table 9. Variation of V/V_o with oxidation time of lube oil without and with prepared compound C_1

Sample	0	24	48	72
0.25%	1	1.085	1.205	1.358
0.5%	1	1.035	1.096	1.096
1%	1	1.061	1.073	1.199
1.5%	1	1.041	1.073	1.114
Oil only	1	1.979	2.655	3.803

Table 10. Variation of ΔTAN with oxidation time of lube oil without and with prepared compound C_1

Sample	0	24	48	72
0.25%	0	0.34	0.82	1.31
0.5%	0	0.26	0.40	0.54
1%	0	0.31	0.73	0.91
1.5%	0	0.35	0.75	0.92
Oil only	0	1.63	4.12	10.52

Table 11. Variation of Log I_o/I with oxidation time of lube oil without and with prepared compound C_1

Sample	0	24	48	72
0.25%	0	0.0149	0.0628	0.1220
0.5%	0	0.0050	0.0257	0.090
1%	0	0.0630	0.0474	0.165
1.5%	0	0.0630	0.059	0.179
Oil only	0	0.0263	0.116	0.3651

Geometric structures of (zinc dibutyldithiophosphate A_1, zinc di isobutyldithiophosphate B_1 and zinc amylisobutyldithiophosphate C_1) are given in Figures (4-9). The calculated quantum chemical indices of E_{HOMO}, E_{LUMO}, and the ΔE (E_{HOMO} - E_{LUMO}) energy gap data are given in Table (12).

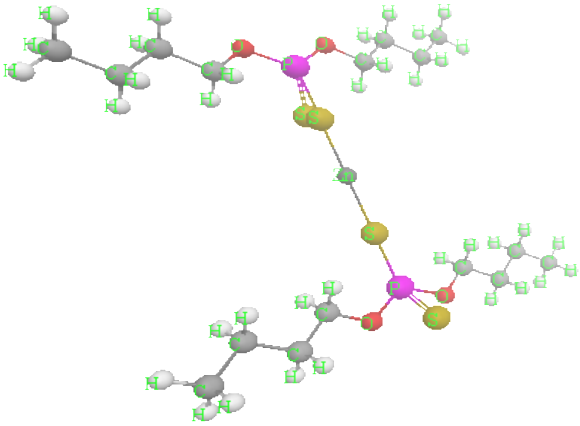


Fig. 4. Optimized structures of A_1

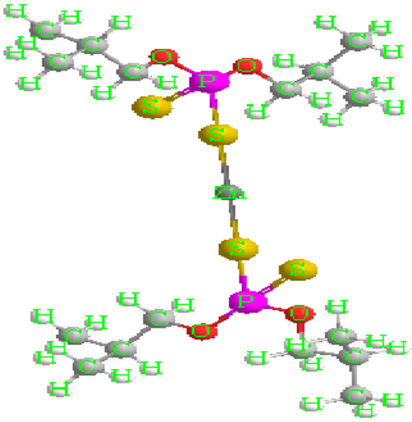
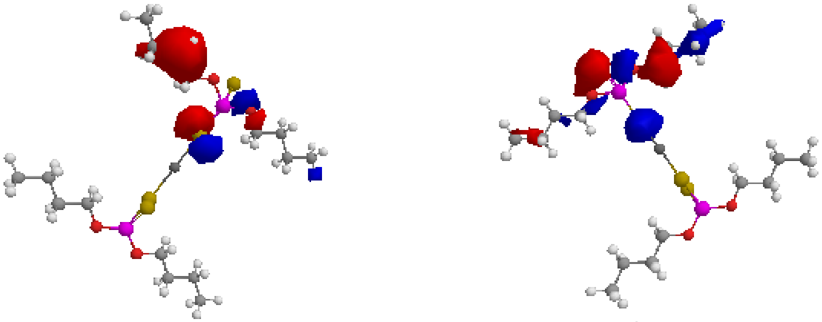


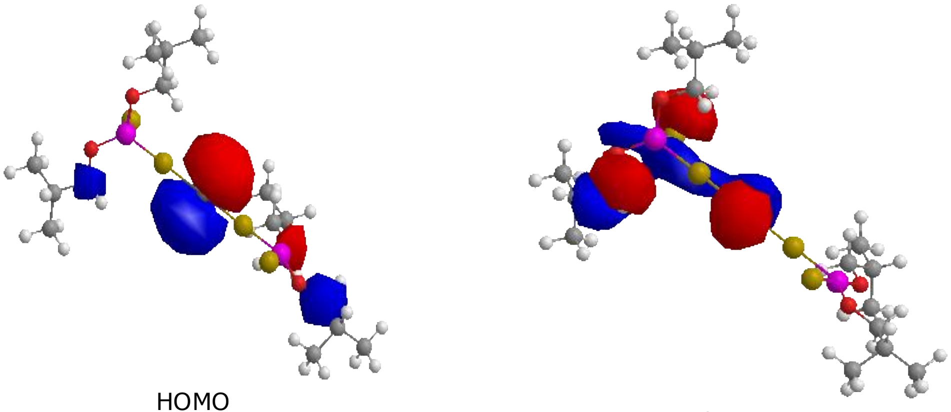
Fig. 6. Optimized structures of B_1



HOMO

LUMO

Fig. 5. The frontier molecule orbital density distributions of A_1



HOMO

LUMO

Fig. 7. The frontier molecule orbital density distributions of B1

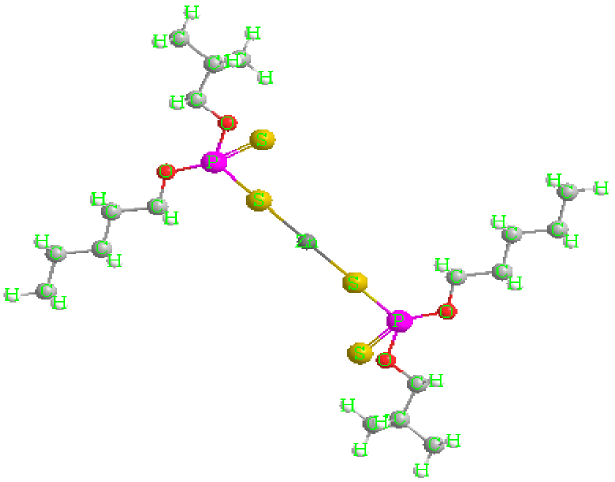
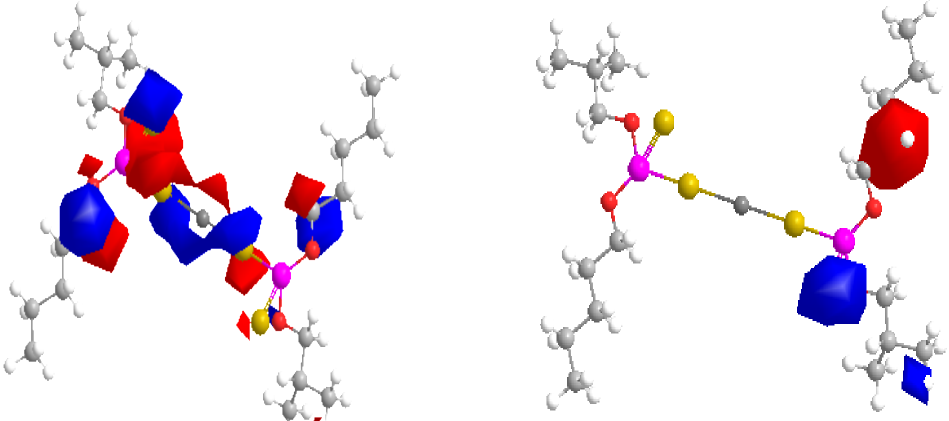


Fig. 8. Optimized structures of C1



LUMO

HOMO

Fig. 9.The frontier molecule orbital density distributions of C1

According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between H_{OMO} and L_{UMO} orbitals of reacting species. Thus, the treatment of the frontier orbitals separately from the other orbitals is based on the general principles governing the nature of chemical reaction. HOMO is often associated with the electron donating ability of a molecule. High E_{HOMO} values indicate that the molecule has a tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbital [16]. E_{LUMO} indicates the ability of the molecules to accept electrons. The lower values of E_{LUMO}, the more probable it is that the molecules to accept electrons. Increasing values of the E_{HOMO} facilitate adsorption and therefore inhibition by influencing the transported process through the adsorbed layer. Low absolute values of the energy gap (ΔE) gives good inhibition efficiencies because the energy required to remove an electron from the last occupied orbital will be low, which facilitate oxidation inhibition process. From the data given in Table (12), it is obvious that the higher value of calculated energy gap (ΔE) obtained by (A_1), while the lower energy gap value (ΔE) was that of (C_1).

Table 12. Quantum chemical parameters

ELUMO) (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	$\Delta E=(E_{HOMO}-E_{LUMO})$ (eV)	Absolute ΔE
A1	6.291	17.409	-11.118	11.118
B1	4.709	10.175	-5.466	5.466
C1	12.123	13.223	-1.1	1.1

That gives good evidence on the obtained efficiency of the studied antioxidant to inhibit the oxidation process. So the inhibition efficiency of C_1 is greater than that of A_1 which is in good compatibility with the experimental results shown in the change of viscosity and total acid numbers. During usage lubricating oils undergo changes termed degradation and contamination, which render them in effective for further application. Lubricating oil goes through normal degradation and about 50% of it is consumed in the process. The rest of the oil picks up a number of contaminants from the working environment such as residual components of engine fuels, solids from wear processes along with corrosion products, dirt, soot, and combustion product etc. degradation involves changes in the desired viscometric properties of oil as a result of alteration in the lubricating oil molecular structure caused by cracking, isomerization and polymerization reactions promoted by high temperatures in the running engine. The overall effect of this degradation is the formation of low molecular weight compounds and oxidation products which include polymerized or condensed molecules called gum and sludge.

The prepared additives (A_1, B_1 and C_1) have been added to lube oil sample sin concentration 0.5wt%, using the centrifuge test method. The percentages of sludge formation during the oxidation of lube oil sample with and without prepared additives are determined and given in Table (13), which confirms the same results of the antioxidant activity [15].

Table 13. Percentage of sludge formation after and before addition of the prepared compound(A_1, B_1 and C_1) at oxidation time (72 h.)

Sample	% of sludge at time 72h
A_1	0.3720
B_1	0.1526
C_1	0.1435
Blank	6.6776

4. Conclusions

1. Three zinc dialkyldithiophosphate compounds were prepared different in chain length.
2. All the prepared compounds were found to be soluble at lube oil SAE-30 free of additives.
3. The structures of the prepared compounds were elucidated by Fourier Transform Infrared Spectroscopy (FTIR), Elemental analysis and Gel Permeation Chromatography (GPC).
4. The efficiency of the prepared compounds as an antioxidant were studied, it was found that all the prepared compounds are efficient as antioxidant and the optimum concentration is 0.5%.
5. The compound C_1 give the best results as antioxidant.
6. The results obtained from calculated quantum chemical were on the same line with the experimental results.

References

[1] Ahmed NS and Nassar AM. Tribology - Lubricants and Lubrication, Chapter 10, pages 249-268, 2011.

[2] Hassan HM, Habib OMO, Moawad EB and El-Bana GG, El Defrawy AM. Synthesis of some novel antioxidant and anticorrosive additives for Egyptian gasoline motor oils. Lubrication Science; 2011; 23(3):119–138.

[3] Hassan HM, Habib OMO, Moawad EB and El-Bana GG. The Synthesis and Evaluation of Some New Multifunction Additives for Egyptian Gasoline Motor Oils. Petroleum Science and Technology, 2011; 29(5): 549-559.

[4] Pederson CJ. Mechanism of Antioxidant Action in Gasoline. Ind. Eng. Chem., 1976; 48(10): 1881-1884.

[5] Ploegmakers HMJ and van Oort WJ. Post-column coulometric generation and cyclic voltammetric identification of the free radical of the antineoplastic agent etoposide (VP 16-213). J. Autom. Chem., 1988;10(3) 135139.

[6] Yang Z, Hollebone BP, Wang Z, Yang Ch and Landriault M. Factors affecting Oxidation Stability of commercially Available Biodiesel Products. Fuel Processing Technology, 2013; 106: 366-375.

[7] Rose DJ. Analysis of Antioxidant Behavior in Lubricating Oils, PhD Thesis, University of Leeds, 1991.

[8] Barnes AM, Bartle KD, Thibon VRA. A review of zinc dialkyldithiophosphates (ZDDPS): characterisation and role in the lubricating oil, Tribology International, 2001; 34(6):389-395.

[9] Sharma V, Erdemir A, Aswath PB. An analytical study of tribofilms generated by the interaction of ashless antiwear additives with ZDDP using XANES and nano-indentation. Tribology International, 2015; 82, Part A: 43-57.

[10] Azman NF, Samion S. Improvement of the Lubrication Performance of RBD Palm Stearin as an Alternative Lubricant under Different Sliding Speeds. Journal of Mechanical Engineering, 2017; 63(1): 15-24, 2017.

[11] Gachot C, Hsu Ch, Suárez S, Grützmacher P, Rosenkranz A, Stratmann A and Jacobs G. Microstructural and Chemical Characterization of the Tribolayer Formation in Highly Loaded Cylindrical Roller Thrust Bearings. Lubricants, 2016; 4(2): 19.

[12] Hasham AI, Abdel El-Azim WM and El-Maadawi NM. Synthesis and Evaluation of Some Antioxidant Additives. Egyptian Journal of Petroleum, 2007; 16(2): 59-80.

[13] Azim AA, Nassar AM, Ahmed NS and Kamal RS: Multifunctional Lube Oil Additives Based on Octadecene-Maleic Anhydride Copolymer. Petroleum Science and Technology,2010; 29: 97 – 107.

[14] Kamal RS, Ahmed NS and Nassar AM. Study the efficiency of some compounds as lubricating oil additives. Journal of Applied Petrochemical Research,2013; 3:1-8..

[15] Nassar AM, Ahmed NS, Abdel-Hameed HS, El-Kafrawy AF. Synthesis and utilization of non-metallic detergent/dispersant and antioxidant additives for lubricating engine oil. Journal of Tribology International,2016; 93: 297–305.

[16] Nessim MI, Osman DI, Attia El-Sayed K, Ebtsam AA and Mohammed HA. The Role of 5-(4-Alkoxybenzylidene)-2-Thioxo-4-Oxo-1, 3-Thiazolidine As Antioxidants for Egyptian Lube Oil Base Stock. Int. J. Curr.Res.Chem.Pharma.Sci.,2015; 2(2): 80–93, 2015.

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