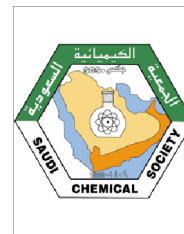




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ORIGINAL ARTICLE

Evaluation of some functionalized imidazoles and 1,2,4-triazoles as antioxidant additives for industrial lubricating oils and correlating the results with the structures of additives using empirical AM1 calculations



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Abstract Functionalized 4,5-diphenyl-imidazoles, 4,5-diphenyl-1,2,4-triazoles and 5-(*o*-hydroxyphenyl)-4-phenyl-1,2,4-triazoles at the 2-position with thiol, thiomethyl and thiobenzyl groups, have been tested as antioxidant additives for lubricating oils. Whereas the thiomethyl groups in such compounds increased the antioxidant property than the thiol group, the corresponding thiobenzyl groups did the reverse. The results can be explained, based on correlating the electron donating and withdrawing abilities of the substituents with the oxidation stability. The triazoles carrying a phenolic hydroxyl group have more antioxidant power than those without such a group. The imidazoles gave the oils more oxidation stabilities than the two types of triazoles with the same functionalities. The 4,5-diphenyl-2-thiomethyl-imidazole (**2**), as an additive, has the highest antioxidant

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Empirical AM1 calculations;
QSAR

property, reaching the level of standard one when its concentration is 1.0% wt. instead of the 0.8% wt. of the standard. The correlation of the antioxidant character of the heterocyclic additives with their structures has been investigated using the semiempirical gas phase AM1 calculations for the studied heterocycles. The relative stability of the imidazoles **1** and **3** compared to **2** were in the order $2 > 1 > 3$. Similarly, the relative stability of the triazoles are in the same order where $5 > 4 > 6$ and $8 > 7 > 9$.

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1. Introduction

The performance of engine oils, turbine, pump, hydraulic and other industrial lubricants is improved by the addition of specific types of additives (El Ashry et al., 2006, 2009; Lange et al., 2001; Li et al., 2003; Brown et al., 2006; Denis et al., 2001; Nakajima and Kawakami, 1999; Burjes and Schroeck, 1994; Farg and Horodysky, 1993; Lam and Liesen, 1990; Vasil'kevich et al., 1977; Duyck et al., 2006; Saito et al., 1996; Germanaud et al., 1990; Kaplan et al., 1970; Vann et al., 2004; Evans, 1992). These additives are oil soluble chemicals and are usually added to prevent the formation/deposition of insoluble materials, oxidation of the lubricant, metal corrosion and other harmful effects due to the use of oil, or caused by its extended storage (Kauffman 1988, 1989, 1994).

The additive-concentrations decrease with time which may be due to the reaction with dissolved atmospheric oxygen. Therefore, the correlation of the additive-concentration of the lubricant with time has been found to be valuable in judging the remaining useful life of the lubricant, and for determining the benefits of adding antioxidants.

More than one antioxidant can be added to the lubricant; the main types of antioxidants are aromatic amines, hindered phenols and their hindered derivatives as well as dithiophosphate derivatives. Most antioxidants function by either decomposing peroxides or by reacting with free radicals. Hindered phenols react with free radicals and prevent polymerization reactions, which would otherwise form insoluble gums. The aromatic amines function similarly but with a different mechanism; the hydrogen-bonded to the nitrogen is readily removed to generate a stable free radical. A combination of the phenolic and amine antioxidants in an additive package enhances the overall antioxidant effect (Puckace and Martella, 1996; Farzaliev et al., 1991; Vasil'kevich et al., 1983; Roberts 1983; Hachisa 1995).

In the present work, some imidazole and 1,2,4-triazole derivatives **1–9**, functionalized with phenolic, thiol, thiomethyl and thiobenzyl groups (Vann et al., 2004; Vasil'kevich et al., 1977) were evaluated as antioxidant additives for industrial lubricating oils. The empirical AM1 calculations were investigated on the studied compounds which were found to agree with the experimental results.

2. Experimental

2.1. Materials

The required compounds were prepared according to the known procedures (El Ashry et al., 2007a,b). Thus, 4,5-diphenyl-2-mercapto-imidazole (**1**), 4,5-diphenyl-2-thiomethyl-imidazole (**2**), 4,5-diphenyl-2-thiobenzyl-imidazole (**3**), 4,5-

diphenyl-3-mercapto-1, 2,4-triazole (**4**), 4,5-diphenyl-3-thiomethyl-1,2,4-triazole (**5**), 4,5-diphenyl-3-thiobenzyl-1,2,4-triazole (**6**), 5-(*o*-hydroxyphenyl)-3-mercapto-4-phenyl-1,2,4-triazole (**7**), 5-(*o*-hydroxyphenyl)-4-phenyl-3-thiomethyl-1,2,4-triazole (**8**) and 5-(*o*-hydroxyphenyl)-4-phenyl-3-thiobenzyl-1,2,4-triazole (**9**) were prepared: structures and melting points are listed in Table 1.

2.2. Formulation of industrial oil blends

Two blends of the turbine oil ISO 46 without and with the recommended dosage (0.8% wt.) of the international commercial antioxidant additive (IA) were formulated and labeled as B0 and B, respectively. The two blends were evaluated according

Table 1 Structures and melting points of the studied compounds.

Compound no.	Structure	Mp (°C)
1		308
2		190–192
3		184–186
4		280–282
5		146–148
6		160–162
7		294
8		188–190
9		192–194

Table 2 Standard test methods for blends.

Properties	Test method
Kinematic viscosity @ 40 °C, mm ² /s	ASTM-D 445
Kinematic viscosity @ 100 °C, mm ² /s	ASTM-D 445
Viscosity index (VI)	ASTM D-2270
Flash point (C.O.C), (°C)	ASTM D-92
Pour point, (°C)	ASTM D-97
A.N, mg KOH/g	ASTM D-664
Foam tendency/stability, ml	IP 146, ASTM D-892
Air release at 50 °C, min	IP 313
Demulsibility after steam treatment, min	IP 19
Copper corrosion (3 h, 100 °C)	IP 154, ASTM D- 130
Rust protection	D-665 B
Oxidation stability (RPT), min	ASTM D- 2272, IP-229
<i>Oxidation stability</i>	
AN value, mg KOH/g	
Sludge content,%	ISO DP 7624

to the international test methods as shown in Table 2, while the results were listed in Table 3.

On the other hand, blends of the tested compounds 1–9 were prepared by dissolving them in a mixture of *N,N*-dimethyl-ethylenediamine and hexyl amine (1:1). Dopanol was added for complete solvation and to achieve the required homogeneity of the final blends. Then industrial lubricating oil blends of percentage dosages of (0.8% wt.) of the tested com-

pounds 1–9 with turbine base oil of viscosity grade ISO 46 were formulated and labeled as B1–B9.

The antioxidant properties of each formulated blend of the tested compounds (B1–B9) were evaluated by applying the oxidation stability tests (RPT) according to D-2272 and ISO DP 7624 test methods; the results were shown in Table 4.

3. Results and discussion

3.1. Evaluation of the formulated industrial lubricating oil blends

The physical, chemical and performance properties of a turbine oil ISO 46 blends B0 and B, without and with the recommended dosage of the international commercial antioxidant additive (IA), were determined and compared with each other. The evaluation was carried out on each blend according to the international standard test methods as maintained in Table 2, and the results were shown in Table 3.

While, different turbine oil blends with viscosity grade ISO 46 were formulated using the recommended dosage 0.8% wt. of each of the tested compounds 1–9 labeled as B1–B9 were evaluated, by applying the oxidation stability tests (RPT) according to D-2272 which is the main property for the antioxidants, also the oxidation stability of the tested compounds were measured according to ISO DP 7624, where, the AN(s) and sludge content were determined for each oxidized blend (Table 4) and compared with a blend of 0.8% wt. of the commercial antioxidant additive IA (B).

Table 3 Physical, chemical and performance properties of turbine oil blends, before and after adding the recommended dosage of commercial additive.

Properties	Standard specifications according to HTGD 90 117 V0001 R (May 2000)	Turbine oil blend ISO 46	
		Without additive B0	With 0.8% wt. (IA), B
Kinematic viscosity @ 40 °C, cSt.	46 ± 10% (41.4–50.6)	46.3	47.00
Kinematic viscosity @ 100 °C, cSt.		6.65	6.75
Viscosity index, VI	90 (min)	94	96
Flash point (C.O.C) °C.	185 (min)	188	189
Pour point, °C	–6 (min)	–3	–6
<i>Foam tendency, ml</i>			
Sequence I	450/0	190/0	60/0
Sequence II	50/0	20/0	0/0
Sequence III	450/0	340/0	50/0
Copper corrosion (3 h, 100 °C)	2 (max)	1 A	1A
TAN, mg KOH/g sample	0.3 (max)	0.015	0.04
Demulsibility after steam treatment	5 (max)	1	1.35
Rust protection	None	None	None
AIR Release, at 50 °C	4 (max)	1.19	1.39
Oxidation Stability, (RPT), min	300 (min)	30	302
<i>Oxidation stability</i>			
A.N. value,mg KOH/g	1.8 max	4.10	1.63
Sludge content, (%)	0.4 max	0.57	0.39

Table 4 Evaluation of the tested compounds.

Blend no.	% Wt. of additive	Oxidation stability (RPT), min, D-2272	Oxidation stability ISO DP 7624	
			A.N value, mg KOH/g	Sludge content (%)
B	0.8% of IA	302	1.63	0.39
B1	0.8% of 1	225	1.65	0.36
B2	0.8% of 2	248	1.55	0.37
B3	0.8% of 3	80	3.35	0.46
B4	0.8% of 4	48	3.88	0.39
B5	0.8% of 5	64	3.8	0.45
B6	0.8% of 6	45	4.1	0.43
B7	0.8% of 7	80	3.4	0.35
B8	0.8% of 8	90	3.32	0.37
B9	0.8% of 9	55	3.68	0.39

Table 5 The optimum dosage of compounds **1** and **2** as antioxidant additives.

Blend no.	Additive % wt.	Oxidation stability (RPT), min, D-2272	Oxidation stability ISO 7624	
			A.N value, mg KOH/g	Sludge content (%)
B1/2	1.0% of 1	228	1.70	0.41
B2/2	1.0% of 2	308	1.75	0.39
B	0.8% of IA	302	1.63	0.39

Table 6 Properties of turbine oil with optimum dosages of 4,5-diphenyl-2-thiomethyl-imidazole **2**, compared with the standard specifications.

Properties	HTGD 90 117 V0001 R	B2/2 (1.0% wt.)
Kinematic viscosity @ 40 °C, cSt.	46 ± 10% (41.4–50.6)	48.03
Kinematic viscosity @ 100 °C, cSt.		6.73
Viscosity index, (VI)	90 (min)	91
Flash point (C.O.C), °C	185 (min)	188
Pour point, °C	–6 (min)	–3
		–6*
<i>Foam tendency/stability, ml, max</i>		
Sequence I	450/0	150/0
Sequence II	50/0	10/0
Sequence III	450/0	80/0
Copper corrosion (3 h, 100 °C)	2 (max)	1A
A.N. mg KOH/g	0.3 (max)	0.02
Demulsibility after steam treatment, min	5 (max)	1.5
Rust protection	None	None
AIR release, at 50 °C, (min)	4 (max)	1.49
Oxidation stability (RPT), min	300 (min)	305
<i>Oxidation stability</i>		
• A.N. value, mg KOH/g	1.80 max	1.75
• Sludge content, (%)	0.40 max	0.39

* With 50 ppm of commercial pour point depressant additive.

The evaluation results of the imidazole derivatives (B1–B2) showed that 4,5-diphenyl-2-mercapto-imidazole (**1**) and 4,5-diphenyl-2-thiomethyl-imidazole (**2**) have the higher oxidation stability for 225 and 248 min respectively, while 4,5-diphenyl-2-thiobenzyl-imidazole (**3**), B3, has 80 minutes only. It was expected that 4,5-diphenyl-2-mercapto-imidazole (**1**) gave a higher oxidation stability due to the ease of the S–H bond breaking but it was found that 4,5-diphenyl-2-thiomethyl-imidazole (**2**), (B2), has a higher stability which could be due to the electron donating nature of the methyl group that facil-

itates the break of the hydrogen-bonded to the nitrogen to generate a stable free radical. This conclusion was confirmed by replacing the methyl group by the electron withdrawing benzyl group as in 4,5-diphenyl-2-benzyl-imidazole (**3**), (B3), that may increase the difficulty of the N–H bond breaking whereby it has a much lower oxidation stability. This conclusion was also valid for the 1,2,4 triazole derivatives, since the methyl group on sulfur in the position **2** in each compound (B5 and B8) increased the oxidation stability compared to the benzyl group (B6 and B9) in the same position. However, the oxidation sta-

Table 7 Calculated (AM1) heat of formation (Kcal mol⁻¹), dipole moments (μ , Debye), HOMO orbital energies (EHOMO, eV), LUMO orbital energies (ELUMO, eV) and charge density on imidazole heteroatoms for the imidazole antioxidants additives **1–3**.

Compound no.	Heat of formation (ΔH_f) Kcal mol ⁻¹	Dipole moment Debye	EHOMO eV	ELUMO eV	Charge density on imidazole heteroatoms
1	103.617	6.425	-8.003	-0.676	(S) -0.266 (N1) -0.236 (N3) -0.236
2	99.07	1.913	-7.938	-0.254	(S) 0.267 (N1) -0.145 (N3) -0.178
3	125.155	1.928	-7.916	-0.3	(S) 0.258 (N1) -0.149 (N3) -0.178

Table 8 Calculated (AM1) heat of formation (Kcal mol⁻¹), dipole moments (μ , Debye), HOMO orbital energies (EHOMO, eV), LUMO orbital energies (ELUMO, eV) and charge density on triazole heteroatoms for the triazole antioxidants additives **4–9**.

Compound no.	Heat of formation (ΔH_f) Kcal mol ⁻¹	Dipole moment Debye	EHOMO eV	ELUMO eV	Charge density on imidazole heteroatoms
4	140.227	5.005	-8.482	-0.358	(S) 0.220 (N1) -0.098 (N2) -0.067 (N3) -0.113
5	134.782	4.697	-8.22	-0.294	(S) 0.312 (N1) -0.102 (N2) -0.068 (N3) -0.116
6	160.893	4.769	-8.189	-0.306	(S) 0.302 (N1) -0.107 (N2) -0.068 (N3) -0.117
7	96.173	4.596	-8.541	-0.422	(S) 0.223 (N1) -0.099 (N2) -0.066 (N3) -0.109
8	90.694	4.501	-8.28	-0.352	(S) 0.314 (N1) -0.103 (N2) -0.067 (N3) -0.113
9	116.799	4.703	-8.246	-0.361	(S) 0.304 (N1) -0.108 (N2) -0.067 (N3) -0.114

bility of compounds **1** and **2** were 225 and 248 min, respectively, which were less than the required standard specifications that must be not less than 300 min. Consequently, the percentages of the tested compounds were raised in the blends (B1/2 and B2/2), as shown in Table 5. Then, the optimum dosage of compound **2**, (B2/2), was found to be 1.0% wt. whereby its oxidation stability became even higher (308 min) than that of the standard (302 min) while the same dosage of compound **1**, (B1/2), did not increase the oxidation stability to the required value.

The physical, chemical, and performance properties of the turbine oil blend 2/2 with optimum dosage of 4,5-diphenyl-2-thiomethyl-imidazole **2**, was compared with those of the stan-

dard specifications according to HTGD 90 117 V0001 R (Table 6), and the poor pour point -3°C was overcome by adding 50 ppm of the commercial pour point depressant additives. The results indicated that the blend 2/2 with the tested compound **2** met all the standard specifications.

3.2. Correlation of the antioxidant character of the heterocyclic additives with their structures

The correlation of the antioxidant character of the heterocyclic additives with their structures has been investigated using the semiempirical gas phase AM1 calculations for the studied heterocycles. Thus, the theoretical calculations were carried out at

the Hartree-Fock level (RHF) using AM1 semiempirical SCF-MO method in the MOPAC 7.0 program (Stewart, XXXX, version 7). All the structures were optimized to a gradient norm of 0.1 in the gas phase. The results of the calculations of heat of formation, relative stability, dipole moments, the highest occupied molecular orbital energies and the lowest unoccupied molecular orbital energies as well as the charge density on the imidazole and/or triazole heteroatoms are given in Tables 7 and 8. The atomic charge density localized on the sulfur atom in each heterocycles 1–9 (Tables 7 and 8) was found to be greater than that on the nitrogen atoms in the imidazole and/or triazole rings. Consequently, the hydrogen directly bonded to the sulfur atom in the thiol tautomer of 1, although the thione one is relatively more stable (El Ashry et al., 2007a,b) and/or to the thioalkyl group (SCH₃, SCH₂Ph) can be easily lost to generate a stable free radical than that linked to the nitrogen atom.

Comparison of the calculated relative stability of the heterocyclic additives led to the conclusion that the thiomethyl heterocycles 2, 5 and/or 8 were the more stable ones (Tables 7 and 8).

The relative stability of imidazoles 1 and 3 compared to 2 were in the order 2 > 1 > 3. Similarly, the relative stability of triazoles are in the same order 5 > 4 > 6 and 8 > 7 > 9.

The order of the above relative stability energy calculations and the electron density measurements were in agreement with the experimental data where thiomethyl imidazole 2 exhibited the higher antioxidant activity. This could presumably be due to the electron donating character of the methyl group compared to H in 1 or its tautomer whereas when the phenyl group is linked to the methyl as in benzyl analog 3, the electron density on the sulfur will again decrease. Thus the stabilization of the generated free radical will depend on the substituent on the sulfur atom.

4. Conclusions

A series of imidazole and triazole derivatives have been evaluated as antioxidants for turbine oils. The results indicated that 4,5-diphenyl-2-thiomethyl-imidazole 2, can be considered as a good antioxidant additive for turbine oils. Moreover the change of substituents on both heterocycles showed parallel influence on the antioxidant stability. Moreover, the antioxidant properties have been shown to improve in such series in a parallel manner with the substituent SMe > SH > SCH₂Ph. The empirical AM1 calculations agreed with the experimental results.

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