

CHAPTER 3

TETRAHYDROPYRAZOLOPYRIDINES AS ANTIFRICTION AND ANTIWEAR AGENTS: EXPERIMENTAL AND DFT CALCULATIONS

The role of lubrication is indispensable in enhancing the durability of critical parts of a machine and making it more energy-efficient [Tung et al. (2004), Verma et al. (2020a)]. A diverse range of lubricant systems has been designed to meet technological advances. Wear, and friction modifiers protect the mating surfaces by a tribochemical film formed *in situ* at the interface. The nature of tribofilm depends on structural properties and concentration of the additives, chemistry at the interface, the temperature at the contact surfaces, sliding speed, and the load applied to the system [Bermúdez et al. (2009)]. A plethora of additives are available in the literature for their wear and friction-reducing properties, such as organic compounds containing heteroatoms [Jaiswal et al. (2014), Kalyani et al. (2014)], inorganic layered structures [Verma et al. (2020b)], metal complexes [Jaiswal et al. (2015)], and nanomaterials [Kalyani et al. (2016), Verma et al. (2018)]. Zinc dialkyl dithiophosphates (ZDDP) are the most versatile additives. Still, their frequent use has been restricted due to their tendency to retard the efficiency of exhaust emission catalytic converters [Xie et al. (2016)]. Several standard norms are available in the literature, where restrictions have been imposed on the limits of sulfur, phosphorus, and sulfated ash contents (SAPS) in the additives [Spikes et al. (2008)] to attain a clean environment.

The high-dispersibility of organic compounds with heteroatoms in typical base oils provides outstanding results. The heterocyclic organic compounds containing nitrogen, oxygen, and sulfur are illustrious in this field owing to their adsorption on the metal surface through lone pair of electrons at the heteroatom and ring electrons of the associated aromatic ring systems. The nature of substituents at the aromatic ring may further modulate electron density at the heteroatoms to facilitate adsorption. An increase in the number of heteroatoms, provided all of them are structurally capable of accessing the metal surface results in enhanced adsorption.

The simple nitrogen and oxygen-containing heterocycles, pyridines [He et al. (2002)], pyrazines [He et al. (2002)], pyrimidines [He et al. (2002)], pyridazines [He et al. (2002)], pyrroles [Kamano et al. (2014)], pyrazoles [Kamano et al. (2014)], imidazoles [Kamano et al. (2014)], oxazoles [Kamano et al. (2014)], oxadiazoles [Kamano et al. (2014)], furans [Kamano et al. (2014)], dioxanes [Kamano et al. (2014)], pyrans [Kamano et al. (2014)], triazines [He et al. (2004), Yang et al. (2013)], tetrazoles [Li et al. (2000)], imidazolines [Xiong et al. (2016)], etc. are reported as effective antiwear agents. Fused benzene ring systems like benzotriazoles [He et al. (2002)], benzoxazoles [Zhang et al. (1999)], benzimidazoles [Xu et al. (2000)], indole [He et al. (2002)], indazole [He et al. (2002)] quinolines [Verma et al. (2019)], quinazolinones [Elkholy et al. (2019)], coumarin [Tang et al. (2021)] have also been studied. However, only a few reports are available on heterocyclic systems where two or more heterocyclic rings are fused [Abdel-Latef et al. (2019)]. Given that hetero atoms play a significant role during the process of adsorption on the metal surface, the increased number of heteroatoms in fused ring systems should enhance the tribological activity considerably.

This instigated us to synthesize substituted tetrahydropyrazopyridines, having two pyrazoles and a pyridine ring arranged in a specific fashion, and evaluate their tribological behavior in paraffin oil on a four-ball tribo-tester using the well-known tribologically active material ZDDP as a reference. The tribo-activity is directly related to the number of adsorption centers accessible to the metal surface. The adsorption of substituted tetrahydropyrazopyridines on the steel surface is anticipated to occur primarily through the nitrogen atoms, provided these are competent enough to approach the surface. The inherent properties of the substituents at the pyridine ring may facilitate adsorption by enhancing electron density at these nitrogen atoms. Density Functional Theory calculations were also performed for a deep insight into electronic environments around adsorption centers. These

calculations have been used to validate the observed tribological results.

3.1. Experimental section

3.1.1. Chemicals

The analytical grade chemicals such as Hydrazine hydrate, ethylacetate, benzaldehyde, *p*-methyl- and *p*-methoxy benzaldehydes, ammonium acetate, ethanol, and acetone were procured from Merck, India. The base lube, paraffin oil (PO), was acquired from Qualigens Fine Chemicals, Mumbai, India. The zinc dialkyldithiophosphate (reference additive) was purchased from Flexsys Chemicals (M) Sdn Bhd, USA.

3.1.2. Synthesis of tetrahydropyrazolopyridine derivatives

2.0 mmol hydrazine hydrate and 2.1 mmol ethyl acetoacetate in ethanol (5 mL) were taken in a round bottom flask. The reactants were stirred for half an hour at 30 °C, and 1.0 mmol aldehyde and 4.0 mmol ammonium acetate were successively added. The prepared reaction mixture was refluxed for 4-8 h and then cooled to room temperature. The 10 mL of distilled water was added, and the mixture was stirred for 30 min [Dabiri et al. (2014)]. The resulting product was filtered, washed with distilled water, followed by acetone, and dried under vacuum (**Fig. 3.1**). NMR spectroscopy was used to characterize the synthesized product. The ¹H and ¹³C NMR spectra of the prepared additives have been provided in the figures(**Fig. 3.2 - Fig. 3.7**). The IUPAC names, abbreviations, structures, and Characterization of the tetrahydropyrazolopyridines are given in (**Table 3.1**).

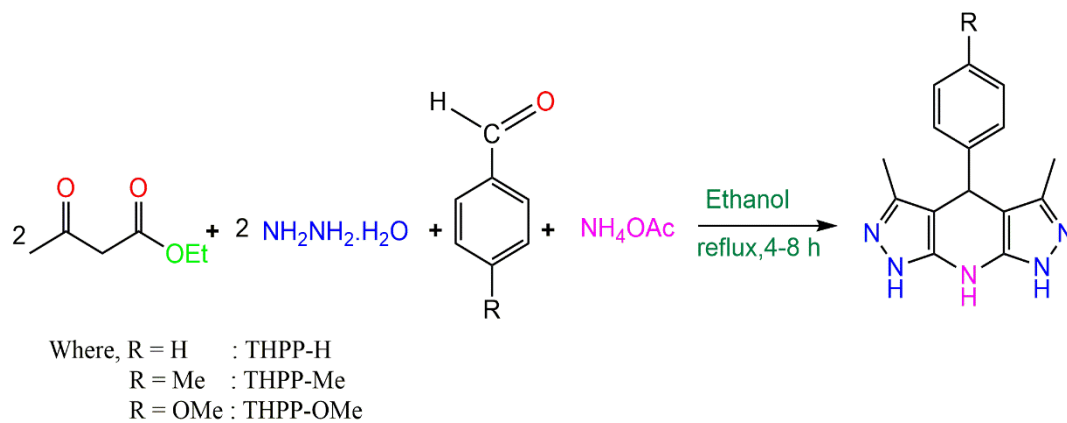


Fig. 3.1. Synthesis of tetrahydropyrazolopyridine derivatives

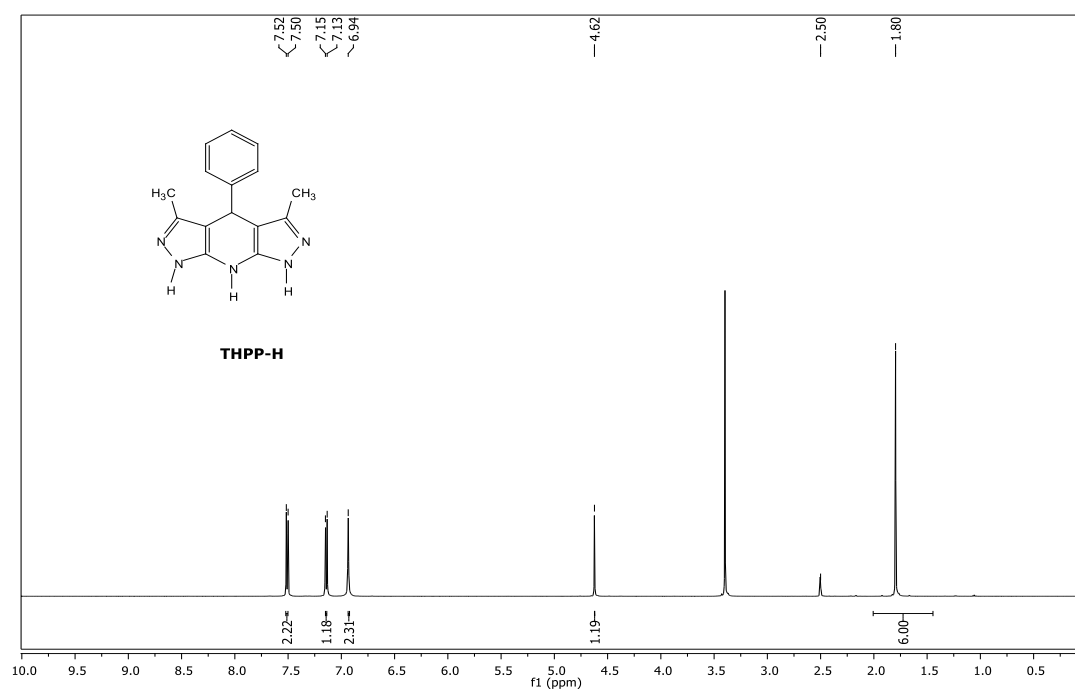


Fig. 3.2. ^1H NMR Spectrum of THPP-H

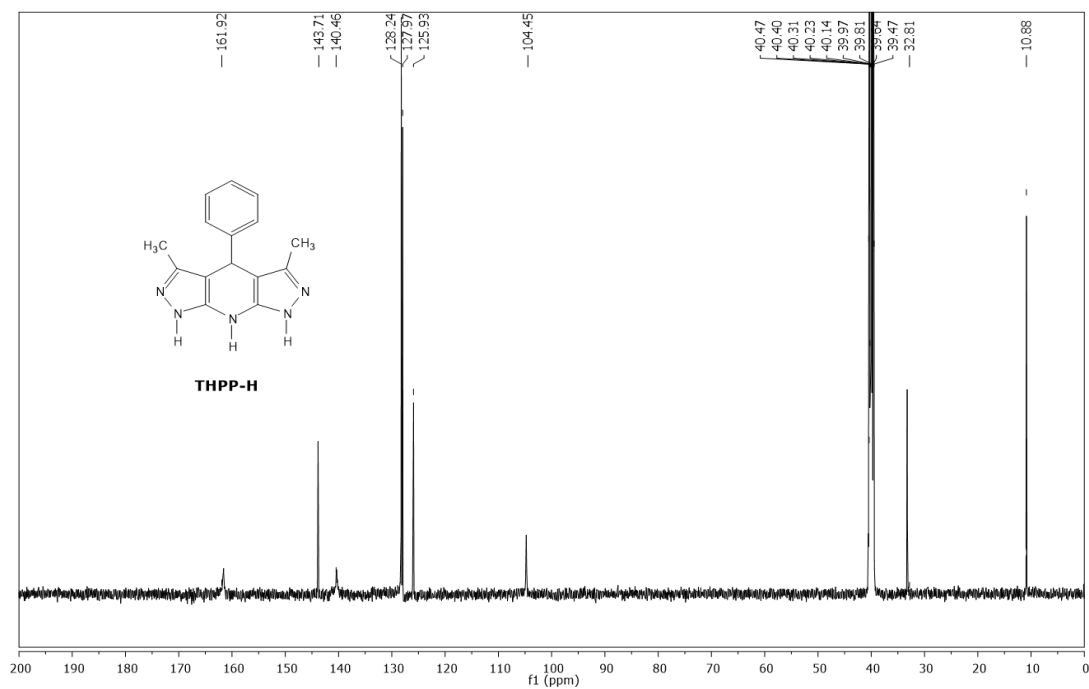


Fig. 3.3. ^{13}C NMR Spectrum of THPP-H

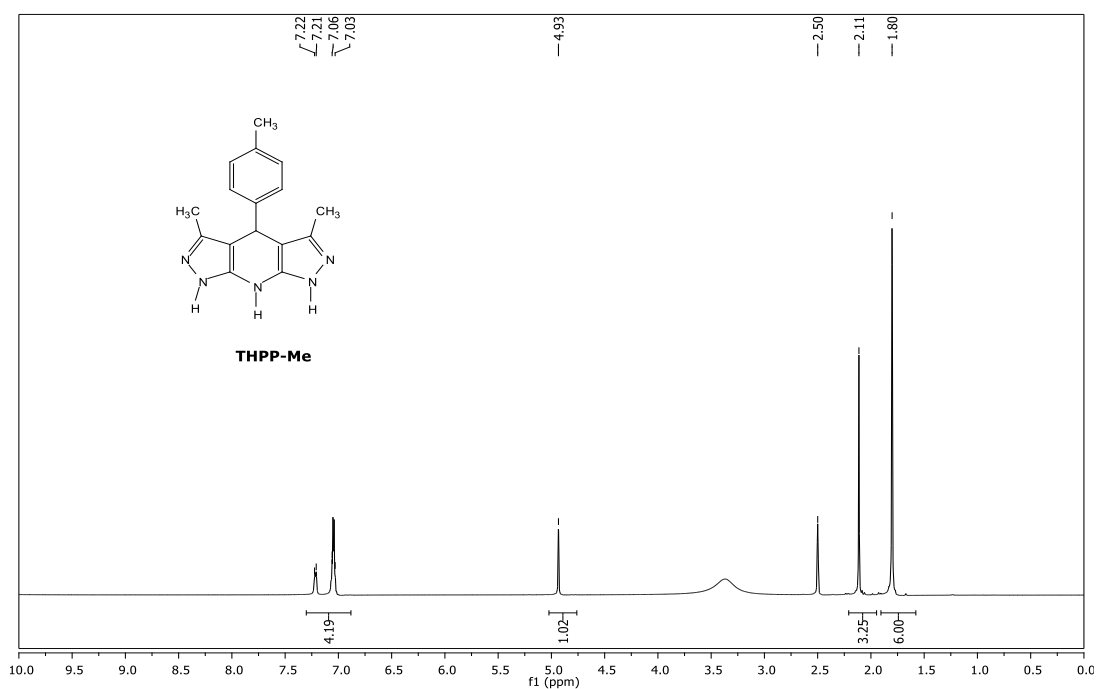
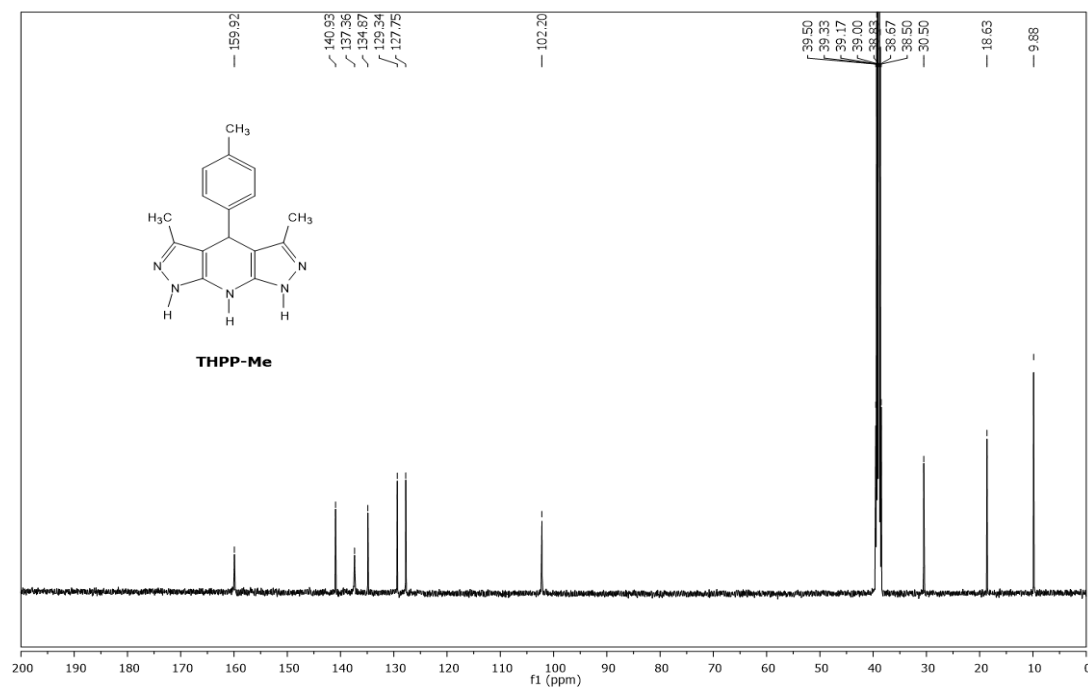
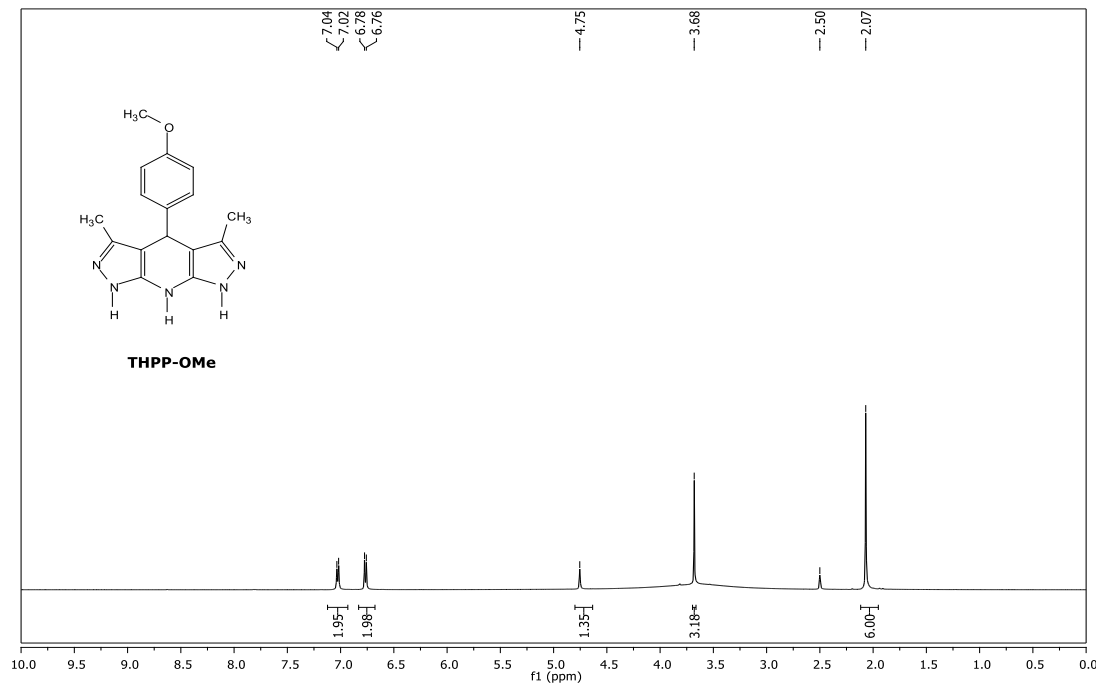


Fig. 3.4. ^1H NMR Spectrum of THPP-Me

Fig. 3.5. ^{13}C NMR Spectrum of THPP-MeFig. 3.6. ^1H NMR Spectrum of THPP-OMe

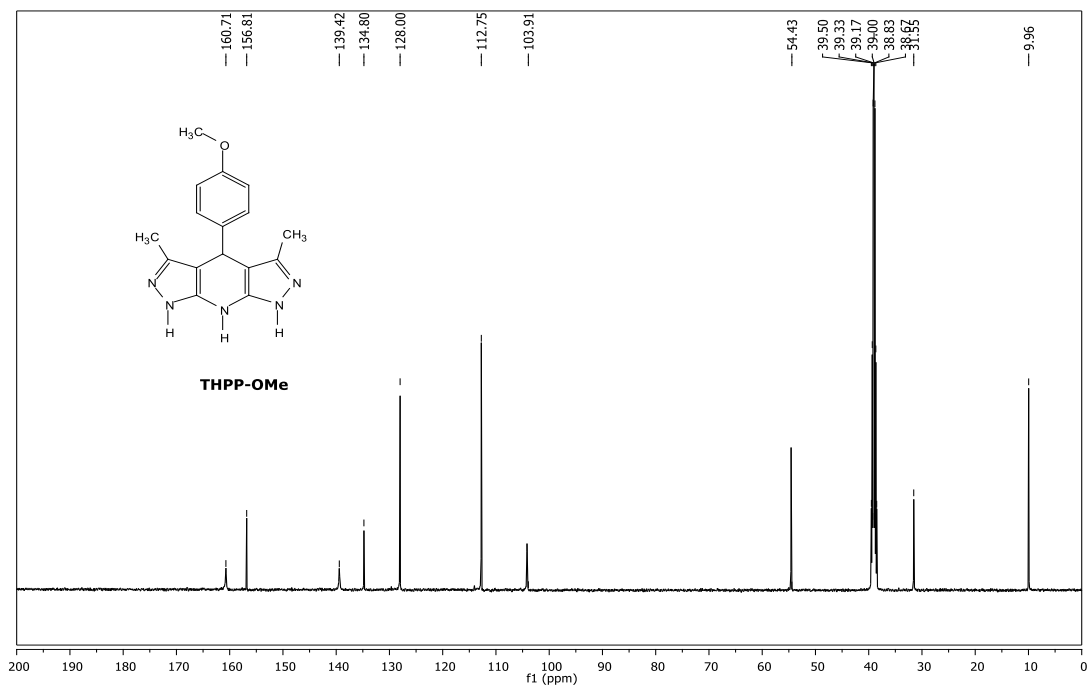
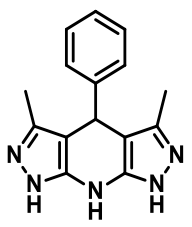
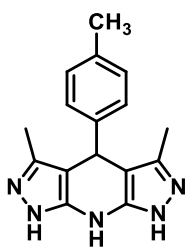
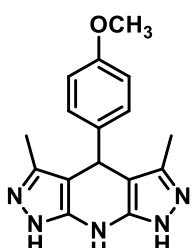


Fig. 3.7. ^{13}C NMR Spectrum of THPP-OMe

Table 3.1. Molecular structures, IUPAC names, abbreviations, and characterizations of the tetrahydropyrazolopyridine derivatives (THPP-H, THPP-Me, THPP-OMe)

S.N.	Structure	IUPAC name and abbreviation	Characterization
1		3,5-dimethyl-4-phenyl-1,4,7,8-tetrahydrodipyrzolo[3,4-b:4',3'-e]pyridine (THPP-H)	Melting point 240-242 °C ¹H NMR (500 MHz, DMSO) 7.52-7.50 (2H, d), 7.15-7.13 (2H, d), 6.94 (1H, s), 4.62 (1H, s), 1.80 (6H, s). ¹³C NMR (126 MHz, DMSO) δ 161.92, 143.71, 140.46, 128.24, 127.97, 125.93, 104.45, 32.81, 10.88.
2		3,5-dimethyl-4-(4-methylphenyl)-1,4,7,8-tetrahydrodipyrzolo[3,4-b:4',3'-e]pyridine (THPP-Me)	Melting point 242-244 °C ¹H NMR (500 MHz, DMSO) δ 7.22-7.21 (2H, d) 7.06- 7.03 (2H, d), 4.93 (1H, s), 2.11 (3H, s), 1.80 (6H, s). ¹³C NMR (126 MHz, DMSO) δ 159.92, 140.93, 137.36, 134.87, 129.34, 127.75, 102.20, 30.50, 18.63, 9.88.
3		3,5-dimethyl-4-(4-methoxyphenyl)-1,4,7,8-tetrahydrodipyrzolo[3,4-b:4',3'-e]pyridine (THPP-OMe)	Melting point 185-186 °C ¹H NMR (500 MHz, DMSO) δ 7.04-7.02 (2H, d), 6.78-6.76 (2H, d), 4.75 (1H, s), 3.68 (3H, s), 2.07 (6H, s). ¹³C NMR (126 MHz, DMSO) δ 160.71, 156.81, 139.42, 134.80, 128.00, 112.75, 103.91, 54.43, 31.55, 9.96.

3.1.3. Tribological analysis

Tetrahydropyrazolopyridine blends in paraffin oil (base oil) with concentrations (0.00, 0.125, 0.25, 0.50, 0.75, and 1.0 % w/v) were made by stirring at 40–50°C for 1-2 h followed by 1h sonication at room temperature. The optimized concentration of the additives was identified as 0.25 % w/v. All tribological tests, therefore, were conducted at the concentration of 0.25 % w/v.

3.1.4. Computational details

DFT computations were performed with the help of B3LYP. Full geometry of the additives was optimized with the standard B3LYP/321G+* basis set applying Gaussian 03, revision C. 01[Dapprich et al. (2004)].

3.2. Results and discussion

3.2.1. Tribological studies

3.2.1.1. Wear and friction studies (ASTM D4172 Test)

The antiwear tests of paraffin oil (PO) with or without synthesized tetrahydropyrazolopyridine derivatives were performed with the help of a four-ball tester. At first, the concentration of the additive was optimized. **Fig. 3.8** displays the deviation in the mean wear scar diameter (MWD) against the concentration of the synthesized additives (0.00 to 1.0% w/v) in base lube at 392N load for 60 minutes. It is obvious from **Fig. 3.8** that compared to plain paraffin oil, the MWD decreases for its blends with tetrahydropyrazolopyridines at all the investigated concentrations up to 0.25 % w/v. Beyond 0.25w/v, there is a sluggish hike in MWD in every case up to 1 % w/v. Although the additives are triboactive at all the tested concentrations, 0.25 % w/v is considered the optimum concentration for testing. It is important to point out that in the case of the commercial additive ZDDP, the MWD is much higher at 0.25 % w/v, and the minimum value is obtained at four times higher concentration, 1 % w/v. **Fig. 3.9** exhibits how COF varies

with time for paraffin oil and its admixtures with various tetrahydropyrazolopyridines for the optimized concentration (0.25% w/v) at load 392 N and 60 min duration. As per the figure, the highest diminution in the coefficient of friction values is noted for THPP-OMe, followed by THPP-Me, and finally, THPP-H.

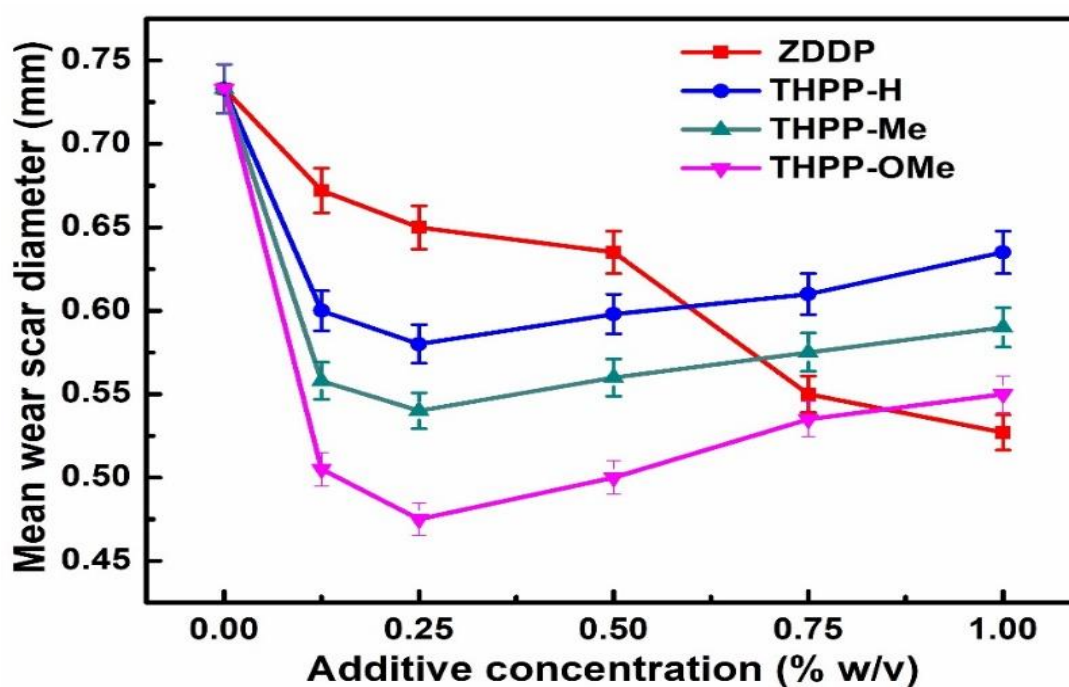


Fig. 3.8. Deviation in mean wear scar diameter with the concentration of ZDDP and different tetrahydropyrazolopyridine additives in PO (ASTM D4172 Test)

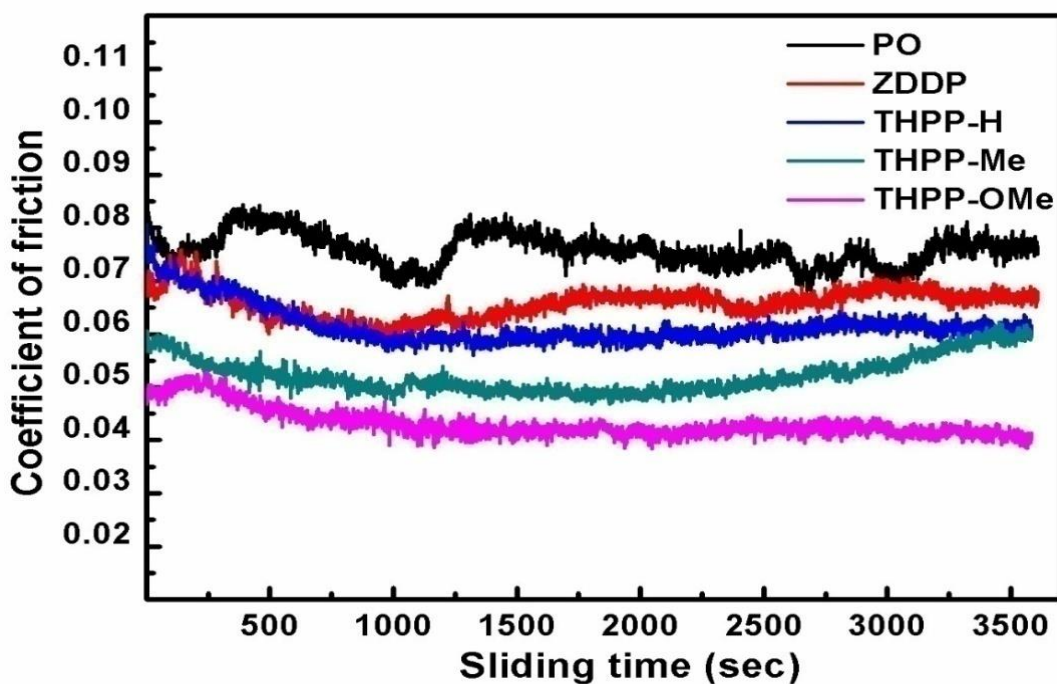


Fig. 3.9. Variation of the coefficient of friction with sliding time in the presence of different additives (0.25% w/v) in PO (ASTM D 4172 test)

Fig. 3.10 displays the magnitude of reduction in MWD and COF data simultaneously for base oil with or without the synthesized additives. The MWD for base oil (0.733 mm) undergoes about 21, 26, and 35% reduction in the presence of THPP-H, THPP-Me, and THPP-OMe, respectively. However, there is only an 11% reduction in MWD for the standard additive zinc dialkyl dithiophosphate (ZDDP). The observed data indicate the highest antiwear performance for the THPP-OMe derivative. Similarly, the reduction in values of the coefficient of friction (COF) of base oil (0.0790) is observable in its blends with ZDDP (14.4%), THPP-H (18.5%), THPP-Me (31.2%) and THPP-OMe (43.5%) supporting the maximum antifriction performance again for THPP-OMe additive.

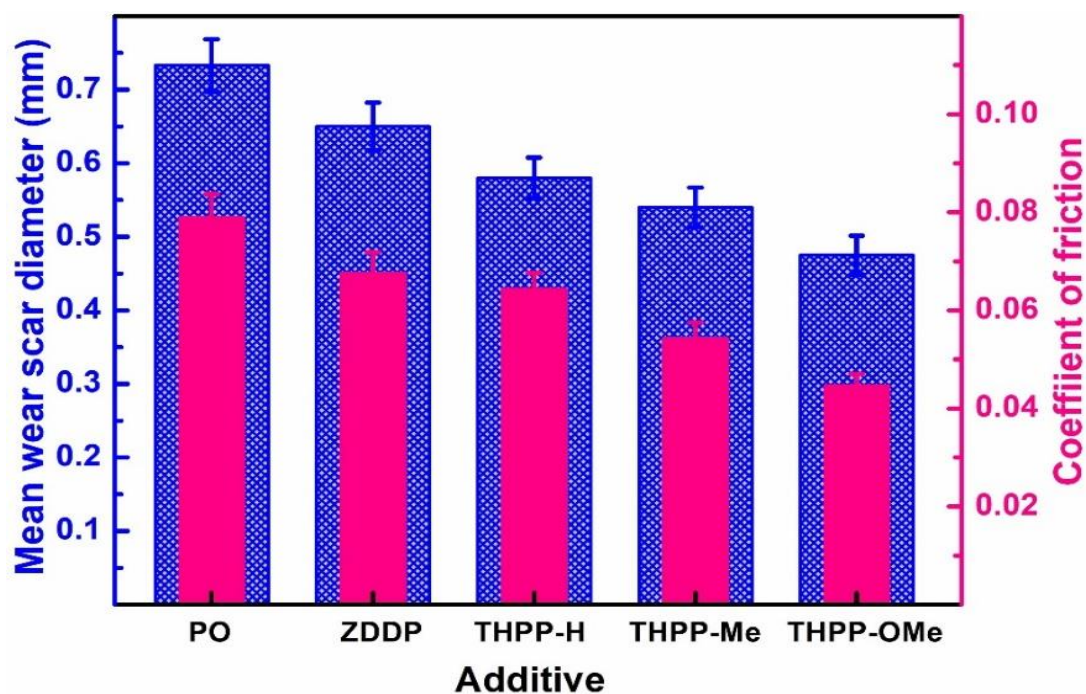


Fig. 3.10. Variation of mean wear scar diameter and coefficient of friction in the presence of different additives in PO (ASTM D4172Test)

3.2.1.2. Load bearing studies (ASTM 5183 Test)

Fig. 3.11 displays the relation between frictional torque and time at succeeding loads of 98 N added at 10 min intervals after the running-in period until seizure load. For the base lube, frictional torque increases slowly up to 1078 N load and, after that, increases abruptly due to failure of the tribofilm. Thus, base oil alone can sustain the load only up to 1078N. It is noticeable that for ZDDP, 0.25% w/v concentration is not compatible with increasing the load-bearing capacity of base lube. On the other hand, for the synthesized additives, a sharp increase in frictional torque is noted at much higher loads, THPP-H (2450N), THPP-Me (2548N), and THPP-OMe (3038 N). Thus, the developed tribochemical film is much stronger to bear the load when THPP-OMe is applied as an additive.

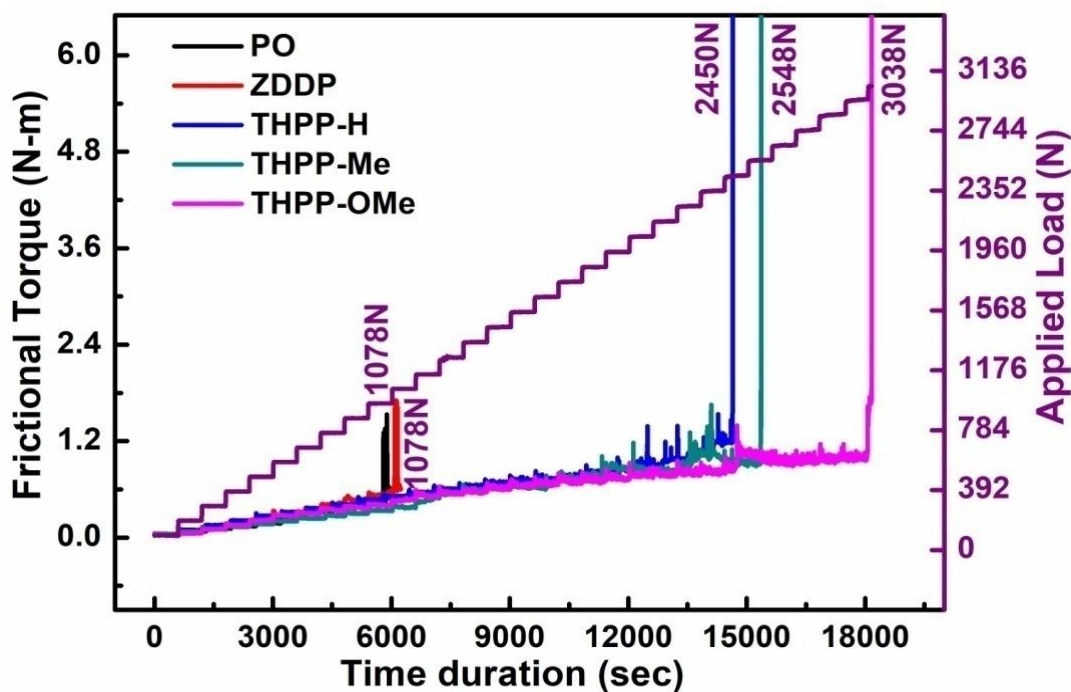


Fig. 3.11. Alteration of frictional torque with stepwise loading and time for different additives (ASTM5183 Test)

3.2.1.3. Frictional power loss

The frictional power loss (P) for different tetrahydropyrazolopyridine additives, collected in **Table 3.2**, has been calculated using the given equation (3.1).

$$P = 221 \times \mu \text{ (watt)} \quad (3.1)$$

Where μ = coefficient of friction

$$1 \text{ kWh} = 3.6 \text{ MJ} \quad (3.2)$$

The PO shows the highest power consumption (0.0628 MJ) as compared to the other additives, ZDDP (0.0537 MJ), THPP-H (0.0512 MJ), THPP-Me (0.0432MJ), and THPP-OMe (0.0355 MJ). The highest percentage reduction in P was observed in the case of the THPP-OMe additive, 43.47 %. Consequently, among all the tested additives, the THPP-OMe additive saves

substantial energy.

Table 3. 2. Loss of frictional power measured for different additives at the concentration of 0.25% (w/v) in PO

S. N.	Additives	Power consumption (MJ)	Reduction in Power consumption	% Reduction in Power consumption
1.	PO	0.0628	—	—
2.	ZDDP	0.0537	0.0091	14.00
3.	THPP-H	0.0512	0.0116	18.47
4.	THPP-Me	0.0432	0.0196	31.21
5.	THPP-OMe	0.0355	0.0273	43.47

3.2.2. Characterization of worn surfaces

The worn surface has been examined by SEM and AFM (contact mode) after the tribological test ASTM D4172. The SEM images of the worn surface on the steel ball in the presence of blank lubricant and its blends with tetrahydropyrazolopyridines (0.25% w/v) are shown in **Fig. 3.12**. The size of the wear scar and its smoothness are directly related to the relative tribological performance of the synthesized additives. Thus, severely damaged wear scar surface for plain paraffin oil while substantially smoothed surface in the case of THPP-OMe may be arguably discussed.

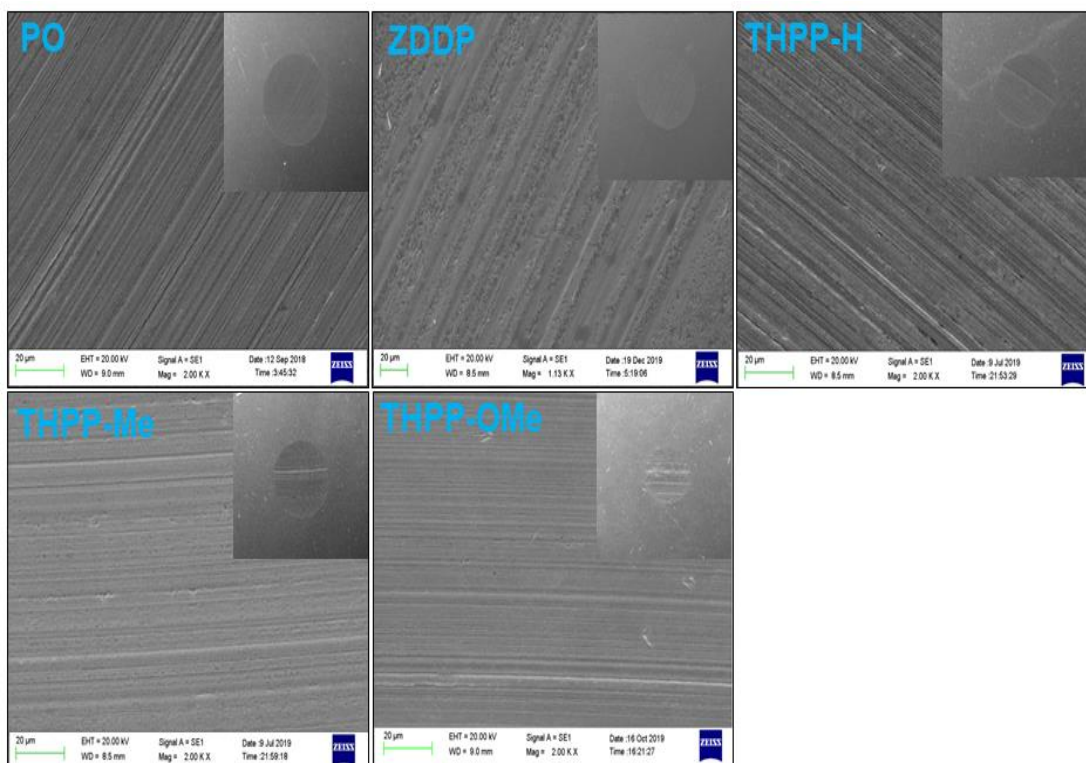


Fig. 3.12. SEM images (inset: full view of wear scar at 100X, wear scar surface at 2.00kX magnification) of the worn steel surface lubricated with PO with or without additives (0.25% w/v) for 60 min test at 392N applied load

The AFM of the worn surface was performed after the antiwear test. The obtained data for surface roughness variables of wear scars on steel balls are displayed in **Fig. 3.13**, together with their 3D AFM figures. The roughness parameters, root mean square area (S_q), and root mean square line roughness (R_q) were found to be very high ($S_q = 674$ nm, $R_q = 670$ nm) for the blank oil. A huge reduction in these values is marked in the presence of additives THPP-OMe ($S_q = 46.98$ nm, $R_q = 37.41$ nm), THPP-Me ($S_q = 59.36$ nm, $R_q = 59.18$ nm), THPP-H ($S_q = 124.77$ nm, $R_q = 120.13$ nm). The above-mentioned values of S_q and R_q validate the order of activity obtained from tribological data.

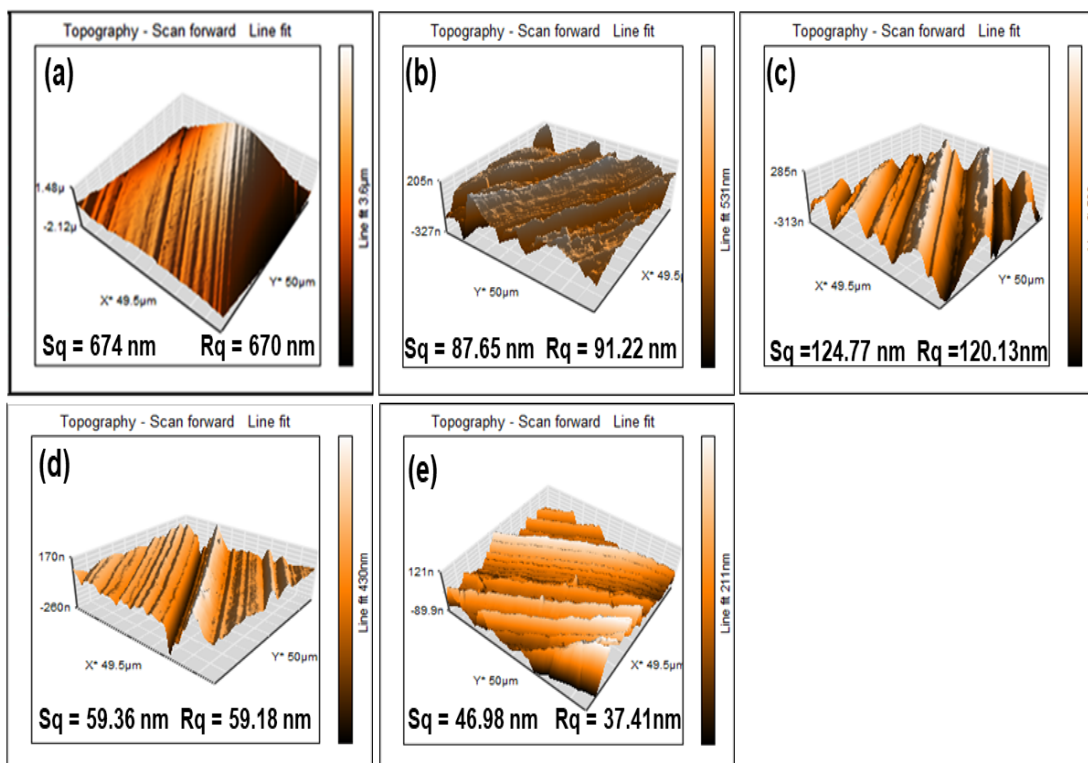


Fig. 3.13. 3D AFM images of the wear scar surface in the presence of PO with or without different tetrahydropyrazolopyridine additives (0.25% w/v) for 60 min test duration at 392N applied load (a) PO, (b) ZDDP, (c) THPP-H, (d) THPP-Me and (e) THPP-OMe

The EDX analysis of wear scar in the presence of plain oil and its admixtures with tetrahydrodopyrazolopyridines has been performed after the antiwear test for elemental characterization of the tribofilm. **Fig. 3.14** shows the EDX spectra of base lube and its admixture with THPP-OMe. The presence of nitrogen as the heteroatom can be easily seen in **Fig. 3.14(b)**, emphasizing its contribution during the development of tribofilm.

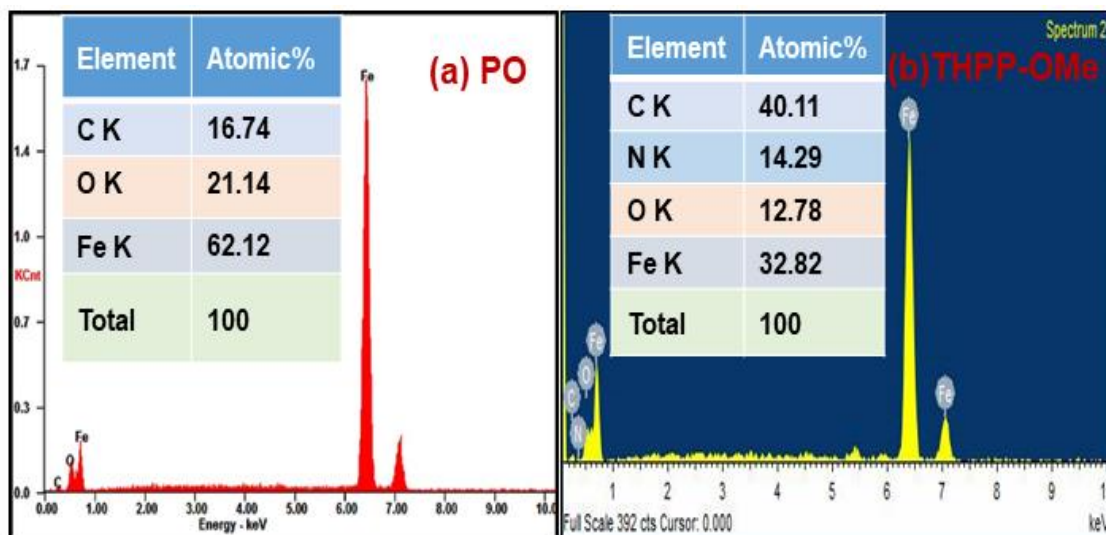


Fig. 3.14. EDX spectra of worn surface lubricated with (a) PO and (b) THPP-OMe

The deconvoluted XPS spectra of C 1s, N 1s, O 1s, and Fe 2p of the tribofilm formed on the wear scar surface in the presence of THPP-OMe after following ASTM D4172 standards are displayed in **Fig. 3.15**. The core-level spectrum of C 1s, **Fig. 3.15(a)** exhibits two peaks at 284.5 and 285.1 eV binding energies corresponding to C-C/C=C, C-O/C-N bonds, respectively [Verma et al. (2018), Kumar et al. (2019), Sordello et al. (2014)]. **Fig. 3.15(b)** shows the core-level spectrum of O 1s, indicating three peaks with binding energies 529.8, 532.1, and 533.5 eV, which could be correlated with Fe-O/Fe₂O₃, C-O, C-O-C moieties respectively [Yang et al. (2011), Yang et al. (2017)]. The N 1s spectrum is illustrated in **Fig. 3.15(c)**. The presence of only one peak identified at 399.9 eV could be accorded with the -N=C/-N-C- group [Jaiswal et al. (2015)]. The binding energies of Fe 2p at 710.8 eV (**Fig. 3.15d**) and O 1s at 529.8 eV (**Fig. 3.15b**) together indicate the formation of iron oxides FeO and Fe₂O₃ confirming oxidation of steel surface iron during rubbing process [Zhou et al. (2001)]. Thus, it may be inferred that the additive adsorbed on the steel surface through heteroatom has decomposed under tribological conditions to form a complex tribofilm along with the mixture of FeO/Fe₂O₃ and

rendered active participation in exceeding lubricating behavior.

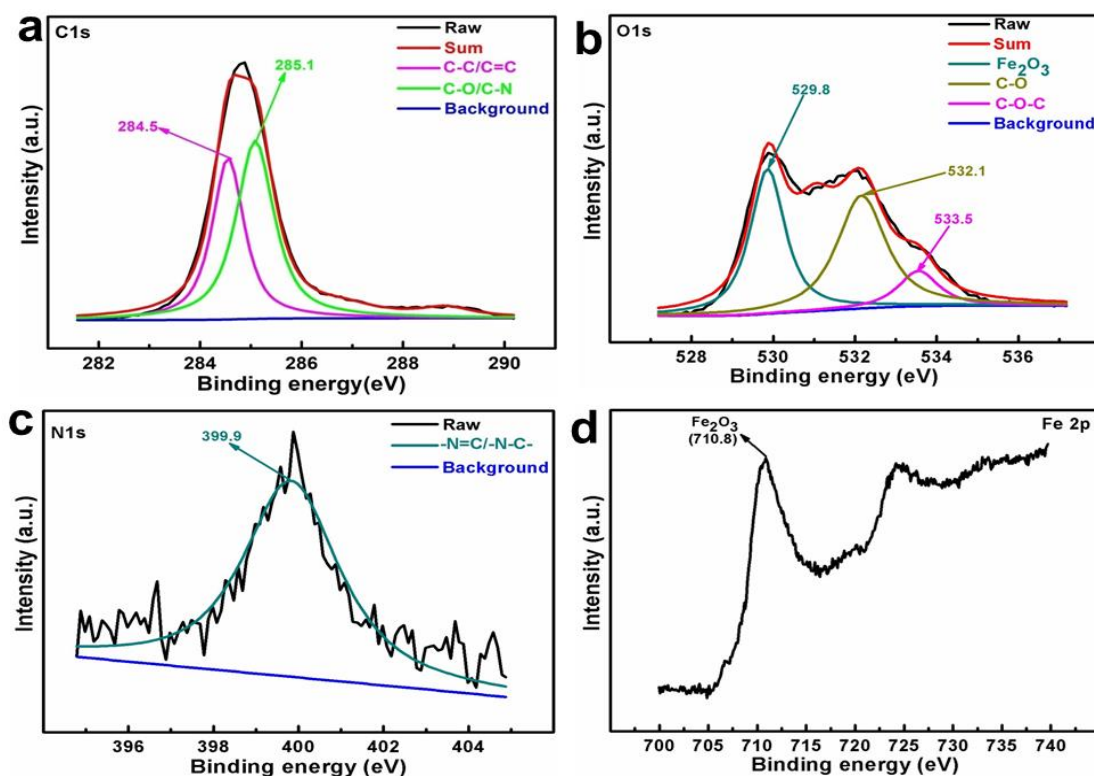


Fig. 3.15. XPS spectra of tribochemical film formed on worn steel surface lubricated with the THPP-OMe additive (0.25 % w/v) at 392 N applied load for 60 min test duration in PO. (a) C 1s (b) O 1s (c) N 1s and (d) Fe 2p

3.2.3. Tribochemistry and proposed mechanism for tribological action

Based on tribological tests, it may be established that tertahyrdopyrazolopyridine formulations prove to be extremely tribologically active. The AFM and SEM results corroborate the experimental data for the relative activity of different additives. The energy-dispersive X-ray analysis provides sufficient evidence in support of heteroatoms present on the tribo-surface. A thin chemical film is formed under the tribo-test condition because of additive decomposition

and interaction of the decomposed products with the mating surfaces. The tenacious film keeps the proximal surfaces away from each other, and therefore, friction and wear are greatly reduced.

3.3. DFT calculations

The DFT calculations have been conducted to observe the effect of various substituents on the inherent framework of tetrahydropyrazolopyridine towards antiwear lubricating properties. An endeavor has been made to correlate the test results with the molecular structures of the synthesized additives. **Fig. 3.16** displays the optimized structures of the synthesized tetrahydropyrazolopyridine additives THPP-OMe, THPP-Me, and THPP-H. At first, the additive molecules tend to undergo physical or chemical adsorption on the steel ball surface via their polar ends, followed by their chemical interaction at the surface. Frontier Molecular Orbital (FMO) theory may give the mechanism of tribological behavior. The quantum chemical variables include total energy, the highest occupied and lowest unoccupied molecular orbitals (E_{HOMO} and E_{LUMO}), and their energy gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) are given in **Table 3.3**. These variables have been used to justify the reactivity of the additive molecules. In accordance with the Hartree–Fock theorem [Zhou et al. (2001), Mourya et al. (2015)], the energies of frontier molecular orbitals are shown by:

$$I = -E_{\text{HOMO}}$$

$$A = -E_{\text{LUMO}}$$

I and A correspond to the ionization potential and the electron affinity, respectively, and are depicted in **Table 3.3**.

Table 3.3. Quantum chemical parameters of tetrahydropyrazolopyridine antiwear additives by B3LYP/3-21G +*

Additives	Fe ₅	THPP-OMe	THPP-Me	THPP-H
Total Energy (a.u.)		-963.67	-888.86	-849.75
E_{HOMO} (Hartree-Fock)	-0.18651	-0.20469	-0.20413	-0.20529
E_{LUMO} (Hartree-Fock)	-0.06420	-0.02943	-0.02859	-0.02951
ΔE (Hartree-Fock)	0.12231	0.17526	0.17554	0.17578
I	0.18651	0.20469	0.20413	0.20529
A	0.06420	0.02943	0.02859	0.02951
χ	0.12535	0.11706	0.11636	0.11740
γ	0.06115	0.08763	0.08777	0.08789
σ	16.35322	11.41162	11.39341	11.37786

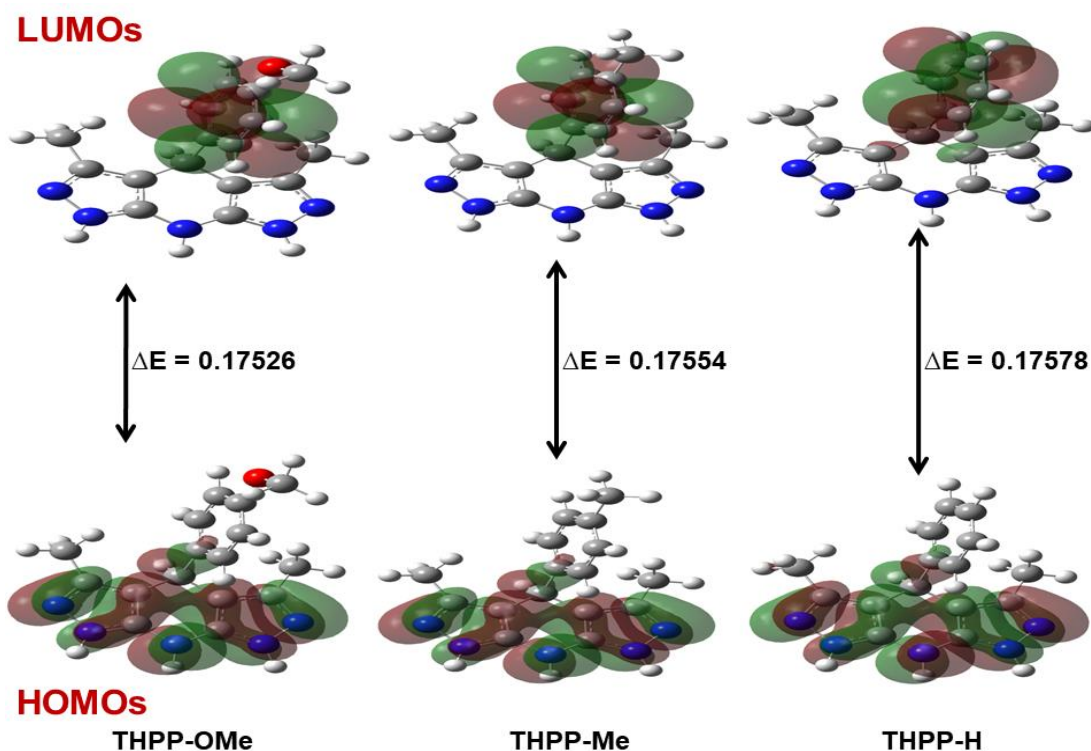


Fig. 3.16. Frontier Molecular Orbitals (HOMO and LUMO) of different tetrahydropyrazolopyridine additives with their ΔE values

The absolute electronegativity (χ) is given as:-

$$\chi = (I + A)/2$$

The global hardness (γ) is equal to:-

$$\gamma = (I - A)/2$$

When metal (iron) and additive come in close proximity to each other, electron flows from lower χ (additive) to higher χ (iron) values until chemical potentials become equal.

The global softness (σ) is defined as:-

$$\sigma = 1/\gamma$$

Global softness (σ) gives information about the reactivity of a compound.

Based on the hardness-softness concept, it may be stated that the highest value for ΔE corresponds to the highest stability index showing hard or inert behavior in a chemical reaction; on the other hand, its lowest value designates the lowest stability index accompanied by soft or easily polarized behavior. The soft additive with the smallest energy gap ΔE is anticipated to show the maximum absorption capability; accordingly, it would be the most tribologically active additive. It is apparent from **Table 3.3** that additive (THPP-OMe) has the lowest value for γ and the highest for σ . Based on these parameters, the ascending order of tribological performance of the synthesized additives may be expressed as-



3.4. Structure-activity relationship

The tribological data for different tetrahydropyrazolopyridines may correlate with their corresponding structures. Structurally, a tetrahydropyrazolopyridine moiety has a pyridine ring fused with two pyrazole rings on either side. It may get adsorbed on the steel ball surface via nitrogens of the pyrazoles and the pyridine ring. All the nitrogens present in a delocalized system are engaged in surface adsorption. The relative performance of different additives is guided by the nature of substituents attached to the benzene ring at the 4th position of the pyridine group. As discussed above, the best activity is displayed by methoxy analog (THPP-OMe) followed by methyl (THPP-Me) and then (THPP-H). The observed order reflects that the electron density on the fused rings has decreased accordingly. The +R effect of the methoxy group and +I effect of the methyl group have been instrumental in increasing the electron-donating tendency of the corresponding tetrahydropyrazolopyridines.

3.5. Conclusions

The additives, tetrahydropyrazolopyridine (THPP-H, THPP-Me, and THPP-OMe), were synthesized and characterized by NMR spectroscopy (¹H and ¹³C). The studied additives

having zero SAPs contents show very high tribological activity at all the tested concentrations. The maximum activity is observed at a very low concentration, 0.25% w/v. Based on antiwear and load ramp tests at 0.25% w/v concentration, the activity of various additives could be established as -



Morphological investigations (using SEM and AFM techniques) of the wear scar surface authenticate the relative tribological activity. The DFT calculations verify the experimentally found order of tribological activity. The EDX analysis of the wear scar surface shows the presence of heteroatoms, nitrogen, and oxygen, confirming the adsorption of different additives on the steel surface. The XPS spectra of the wear scar surface confirm that tribochemical film comprises decomposed products of the additive along with iron oxides.