SUPPLEMENTARY INFORMATION FILE

ON

Tetrahydropyrazolopyridines as antifriction and antiwear agents: Experimental and DFT calculations

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1 Characterization of additives was performed by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. The NMR spectra of additives are given below.

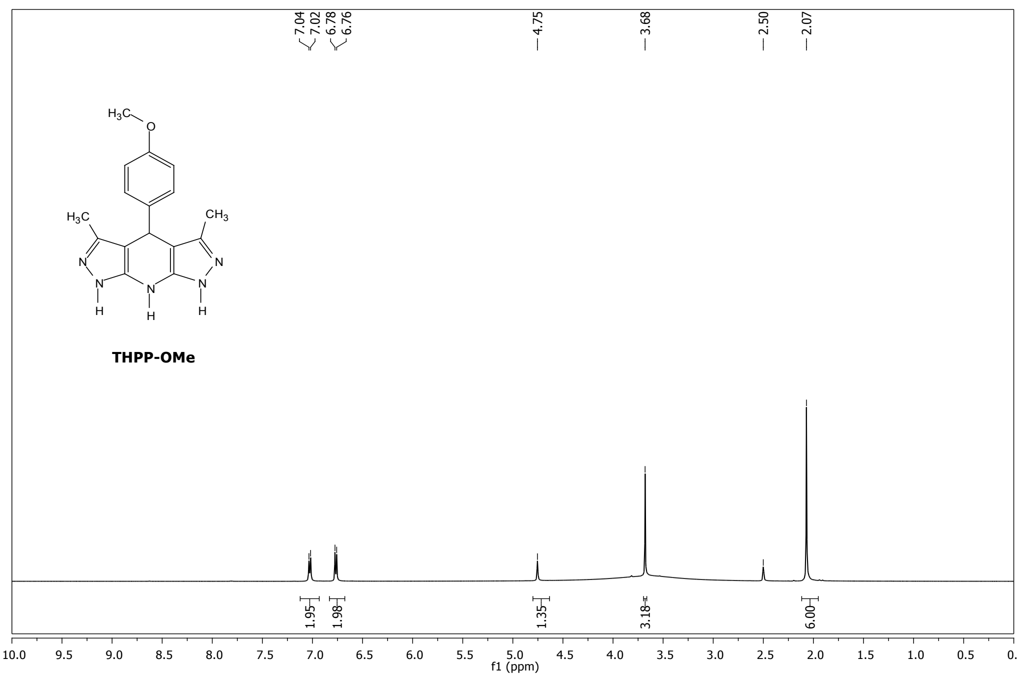

Fig. S1.^{1}H NMR Spectrum of THPP-OMe.

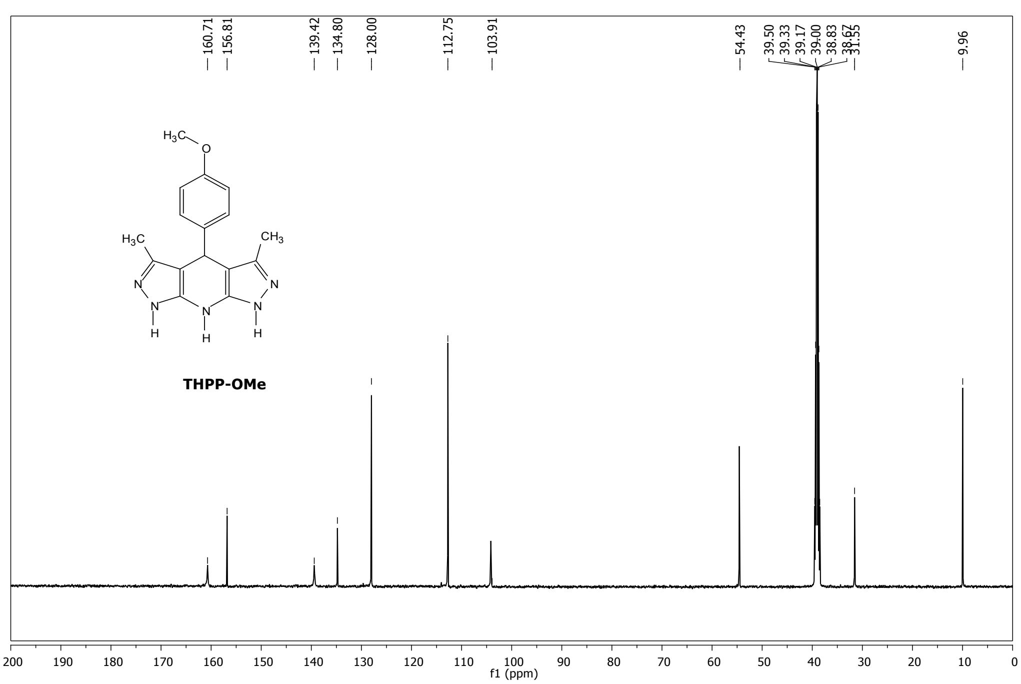

Fig. S2. ^{13}C NMR Spectrum of THPP-OMe.

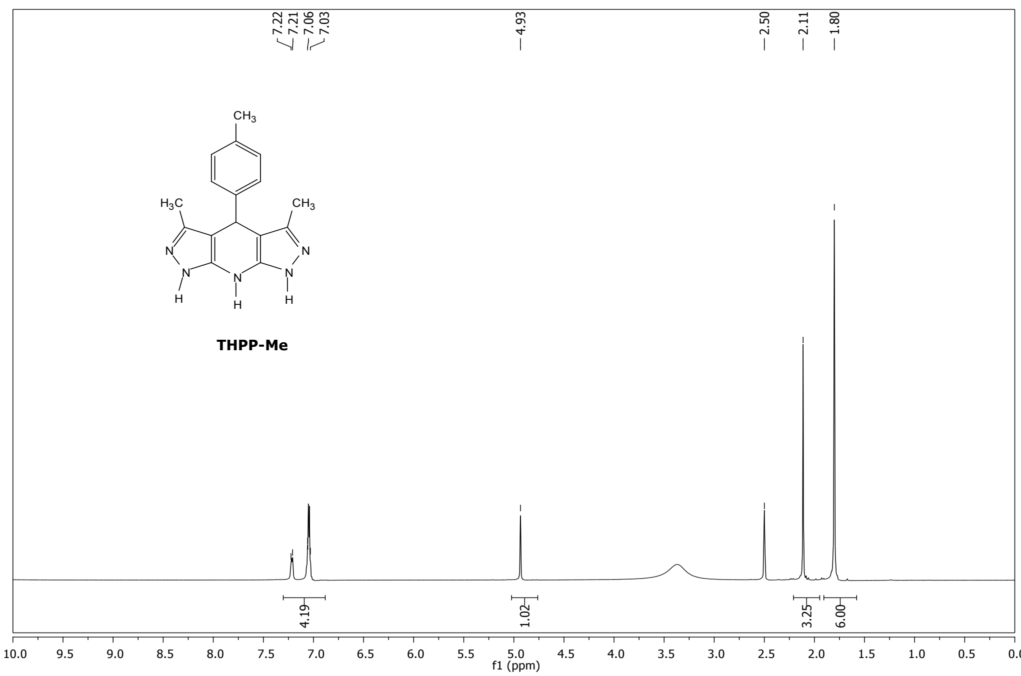

Fig. S3. [1]H NMR Spectrum of THPP-Me.

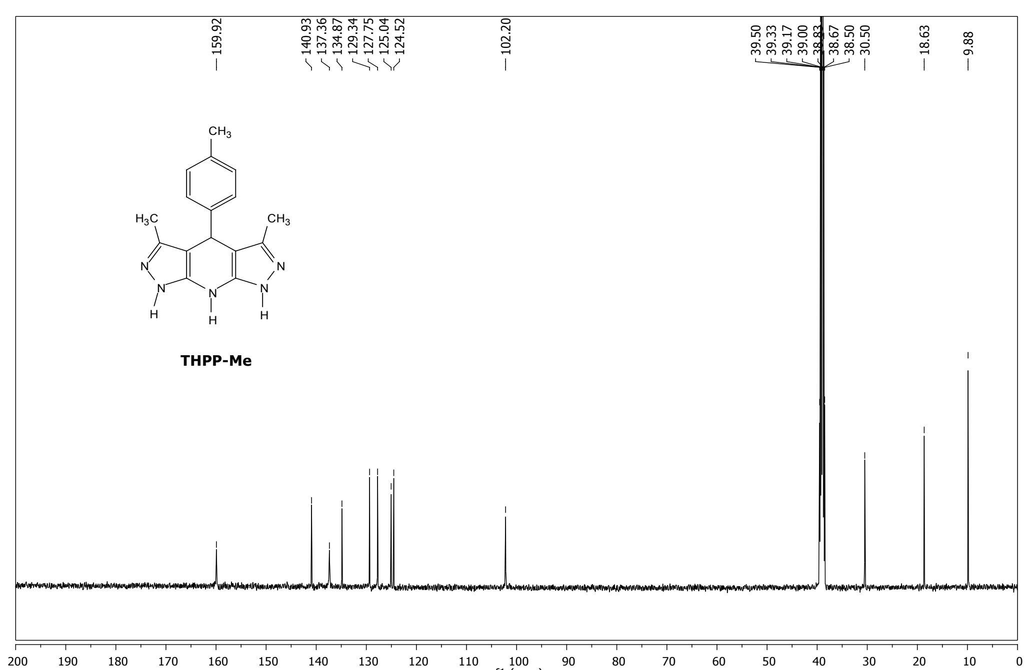

Fig. S4. [13]C NMR Spectrum of THPP-Me.

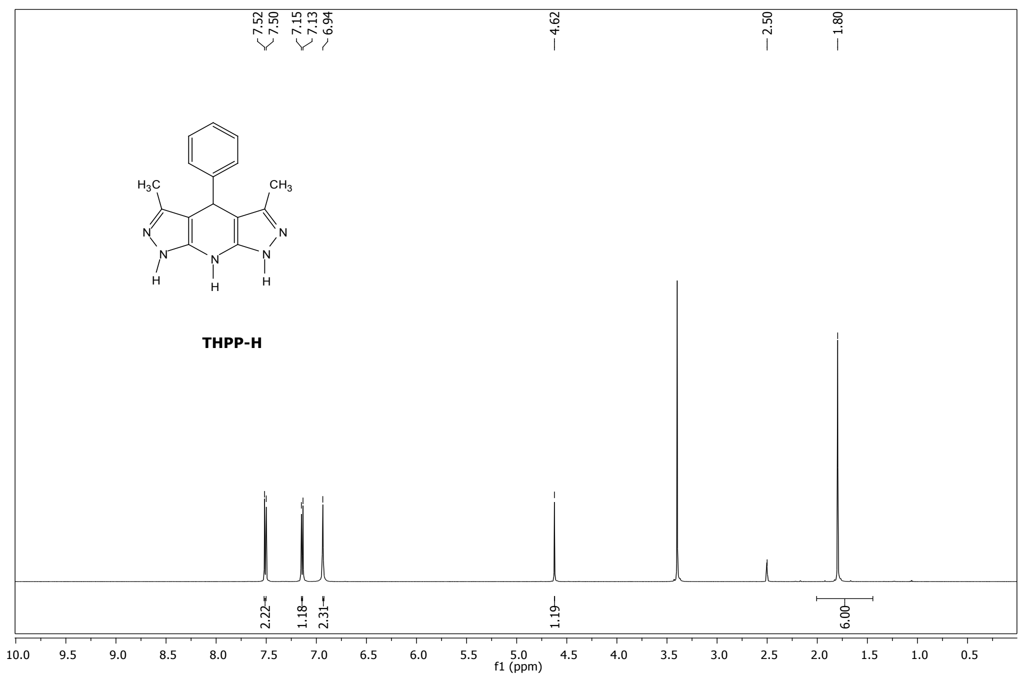

Fig. S5. ^{1}H NMR Spectrum of THPP-H.

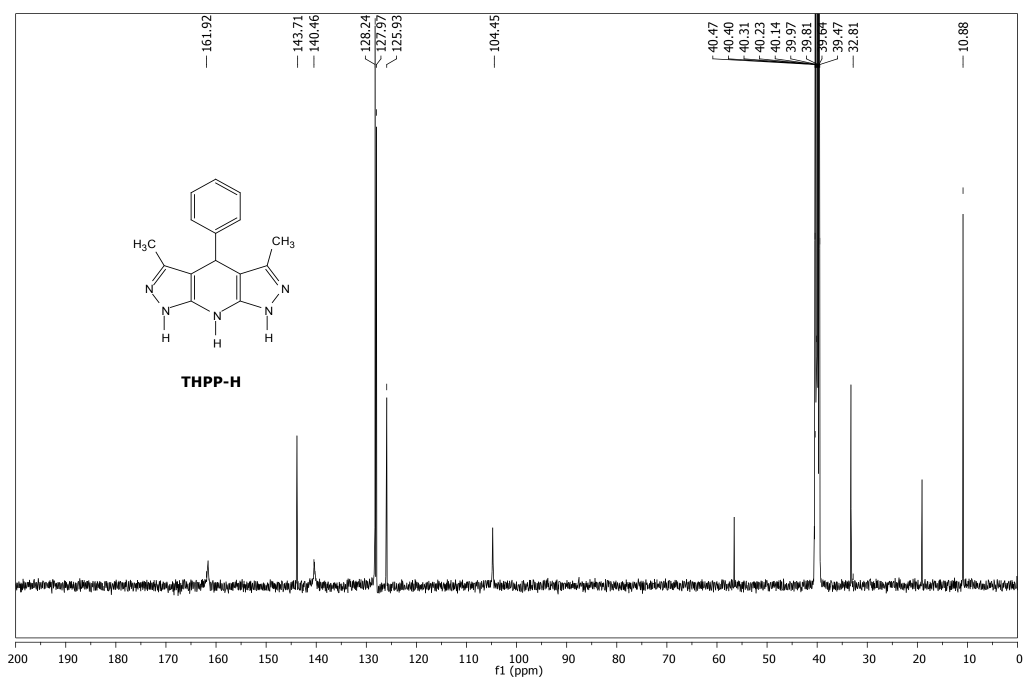

Fig. S6. ^{13}C NMR Spectrum of THPP-H

2 Experimental details

2.1 Tribological Parameters

For each experiment arithmetic mean of the diameter of each ball (d_1, d_2 and d_3) was taken as given by equation [1]. The wear scar diameter was measured with the help of the image acquisition system on the 3 stationary balls, and the wear scar mean value is revealed as mean wear scar diameter (MWD).

2.1.2 Mean wear scar diameter (MWD)

$$d = \frac{d_1 + d_2 + d_3}{3} \qquad [1]$$

2.1.3 Friction coefficient (μ)

The coefficient friction for different antiwear additives was calculated from the pattern observed on the friction paper with the help of equation [2].

$$\mu = \frac{0.222F}{r} \cdot \frac{L}{P} \qquad [2]$$

$$\frac{L}{P} = 0.628$$

r = 0.367 mm

$$F = \frac{springcons\tan t}{6} \times Y$$

Where F = Friction force in kgf exerted on the indicator spring

L = Length in mm of the torque-level arm

r = Distance of contact surface of balls from the axis of rotation (0.367 mm)

Y = Displacement after 2.5 s from the baseline

Value of spring constant up to 80 kgf is 0.226 kgf/cm

2.2 Antiwear Testing

Properties of liquid paraffin oil

The lubricating base oil, neutral liquid paraffin oil (Qualigens Fine Chemicals, Mumbai, India) having specific gravity 0.82 at 25 ^oC, kinematic viscosity, at 40 ^oC and 100 ^oC, 30 and 5.5 cSt respectively, viscosity index 122, cloud point -2 ^oC, pour point -8 ^oC, flash point 180 ^oC and fire point 200 ^oC ,was used without further purification.

The balls of 12.7 mm diameter made of AISI 52100 steel alloy possessing hardness 59-61 HRc were utilized for tribological tests. Before and after each test, balls were rinsed well with *n*-hexane and then properly air-dried.

The prepared admixtures were sonicated for 1hour at RT. The antiwear tests of the synthesized additives were carried out with the help of a Four-Ball Lubricant Tester (Ducom Instruments Pvt. Ltd., Bangalore, India) followed by ASTM D4172. At first, concentration optimization tests were carried out for base oil with and without different concentrations of the studied tetrahyrdopyrazolopyridine additives according to ASTM D4172 norms (applied load, 392 N; sliding speed, 1200; rpm, temperature, 75^oC). All tribological tests were conducted at the optimized concentration (0.25% w/v) under similar conditions. Step loading test was conducted in accordance with ASTM D5183 standards. After the running-in period is over under the test conditions (applied load, 392 N; sliding speed, 600; rpm, temperature, 75^oC and optimized concentration (0.25 % w/v), increments of 98N load were added after every 10 min until the seizure of tribo-surface was noted. In general, all the tribological testing was repeated 3 times.

2.3 Surface analysis

Scanning electron microscopy (SEM) with Energy-dispersive X-ray spectroscopy (EDX) was applied for providing surface magnified images of wear scar of 12.7 mm diameter steel balls and elemental compositions of tribofilm formed on the wear scar respectively using a scanning electron microscope (ZEISS SUPRA 40 electron microscope). A contact mode atomic force microscope (Model no. BT 02218, Nanosurf easyscan2 Basic AFM, Switzerland) was used to investigate the roughness of the worn surfaces with the Si_3N_4 cantilever (Nanosensor, CONTR type) having a spring constant of approximate 0.1 Nm^{-1} and tip radius more than 10 nm. X-ray photoelectron spectroscopy (K-alpha X-ray photoelectron spectrometer) was used for analyzing the chemical composition of the tribofilm formed on the worn surface.

3 Frictional power loss

The frictional power loss has been calculated from antiwear tests using the following relationship

P = T.ω [3]

Where P is the frictional power loss ($N.m.s^{-1}$), T is frictional torque and ω is the angular velocity (rad/sec).

Frictional torque T (N. m) =F. r; F = Frictional force and r= frictional radius= 3.662×10^{-3} (m)

Frictional force F= μ.N; μ = coefficient of friction and N = contact load on the three balls

N = 1.22475L; L is applied load (392 N)

Now T=μ. N .r

ω= πdn/60; d frictional radius = 2r and n=1200 rpm

Substituting all values in Eq. [3], the frictional power loss is

$P = 2.07 \times \mu \times 10^{-3}$(W) [4]

1 kWh = 3.6 MJ [5]

The antiwear test was performed under a load of 392 N at 1200rpm for 1h using a four-ball tester. The total sliding distance of 1.656 km was covered during each test run.