

Supporting Information

Effect of Incorporation of POSS compounds and phosphorous hardeners on Thermal and Fire Resistance of nanofilled Aeronautic Resins

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Characterization

Proton, Carbon 13 and Phosphorous 31 Nuclear Magnetic Resonance (^1H , ^{13}C and ^{31}P NMR) to check the structure of the compounds were used. Samples were dissolved in deuterated solvents DMSO- d_6 . NMR spectra were obtained on a Bruker Spectrometer Avance 400. ^1H and ^{13}C NMR spectra were referred to tetramethylsilane (TMS) and ^{31}P NMR spectra were referred to H_3PO_4 .

Synthesis of bis(3-aminophenyl) methyl phosphine oxide (BAMPO)

In this section we describe the synthesis procedure of bis(3-aminophenyl) methyl phosphine oxide as flame retardant containing phosphorous to be used in epoxy resins for aeronautic applications. Bis(3-aminophenyl) methyl phosphine oxide **4** (BAMPO) was synthesized through a published sequence [1] following three sequential steps applying some modifications. In Figure S1 the scheme of the sequence is reported.

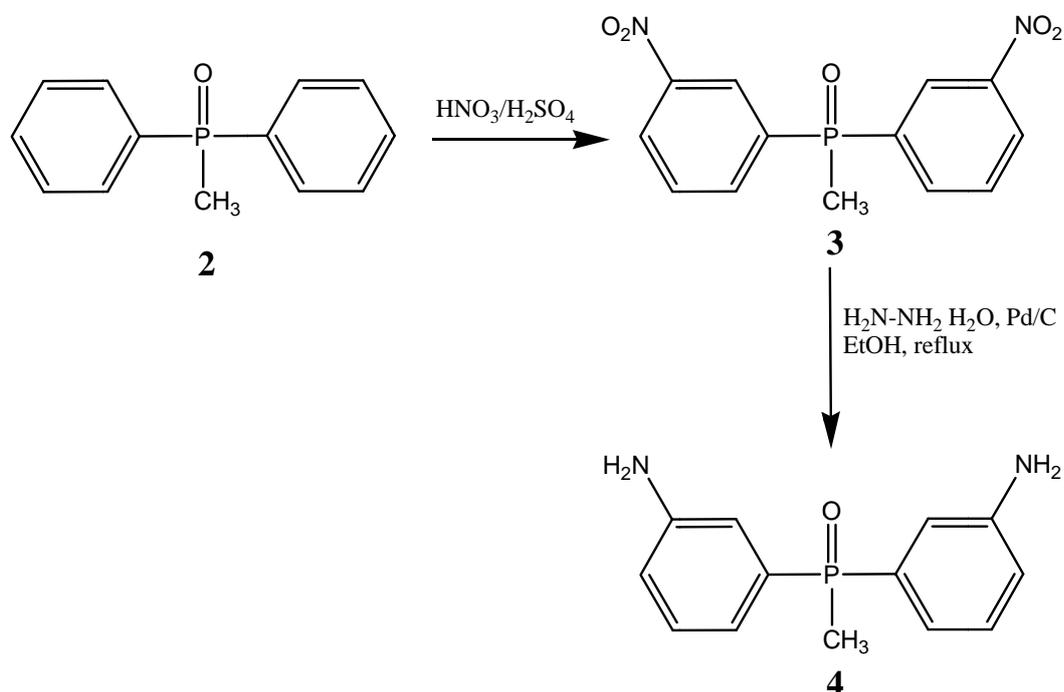


Figure S1. Scheme of synthesis of bis(3-aminophenyl) methyl phosphine oxide (BAMPO).

1st step: preparation of biphenyl methyl phosphine oxide 2

In Figure S2 the scheme of synthesis of biphenyl methyl phosphine oxide **2** is shown.

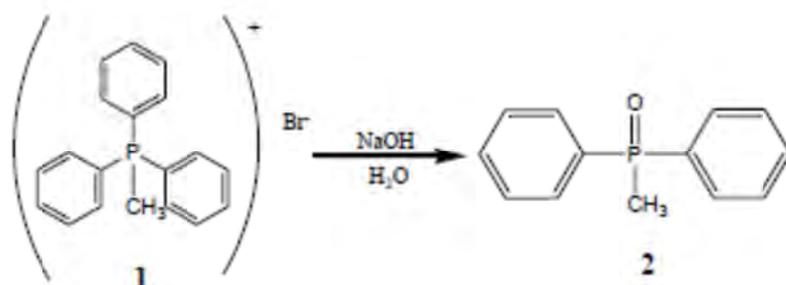


Figure S2. Scheme of synthesis of biphenyl methyl phosphine oxide **2**.

Methyltriphenylphosphonium bromide (10 g, 0.028 mol) was charged in a 250 ml two necked round bottom flask, equipped with a reflux condenser and a magnetic stirrer. Water (50 ml) was then added and the mixture was heated (120°C) to reflux until the starting material was dissolved (about 30 minutes). Meanwhile sodium hydroxide (5.6 g, 0.14 mol) was dissolved in 50 ml of water in a beaker and then transferred to the mixture and further refluxed for two hours. After the addition of sodium hydroxide solution a slightly yellow organic layer was observed on the top of the mixture. The completion of the reaction was monitored by TLC (chloroform: methanol_ 9:1). The coarse product was extracted with chloroform and then washed several times with water. The washed product was dried over a night on magnesium sulfate. Chloroform was removed under vacuum, obtaining 5 g of a white powder. The yield was of 82%.

^1H , ^{31}P , ^{13}C , NMR spectra confirmed the structure (Figures S3-S4-S5):

^1H NMR (^1H (400 MHz, DMSO- d_6 ,ppm): d 7.77-7.73 (4H), 7.66-7.55 (6H), 2.02 (d,3H);

^{31}P NMR (161.97 MHz, DMSO- d_6 , ppm) shown a single peak (32.8);

^{13}C (100 MHz, DMSO- d_6 ,ppm): d: 135.6-134.7 (d,J(C,P), 131.4 (s), 130.1(s), 128.5 (s), 16.2-15.5 (d,J(C,P).

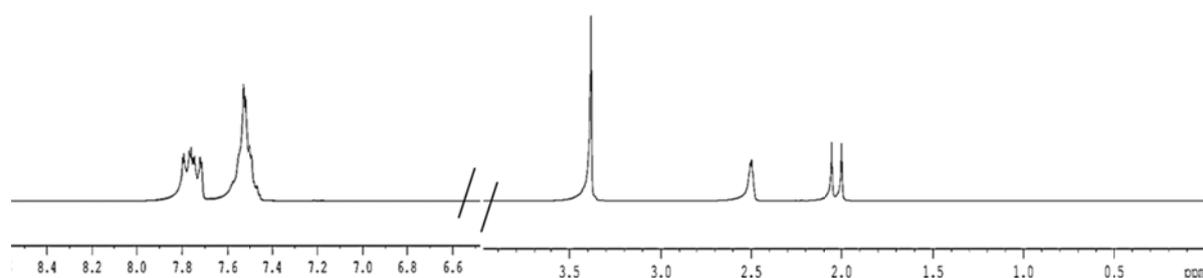


Figure S3. ^1H spectrum of biphenyl methyl phosphine oxide in DMSO- d_6 .

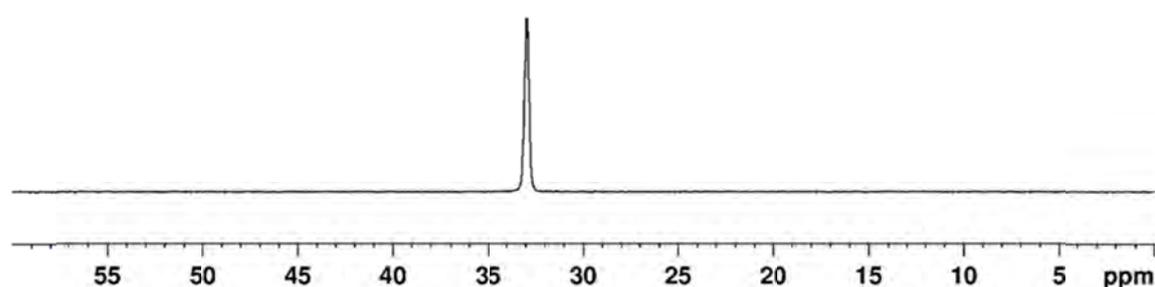


Figure S4. ^{31}P spectrum of biphenyl methyl phosphine oxide in DMSO- d_6 .

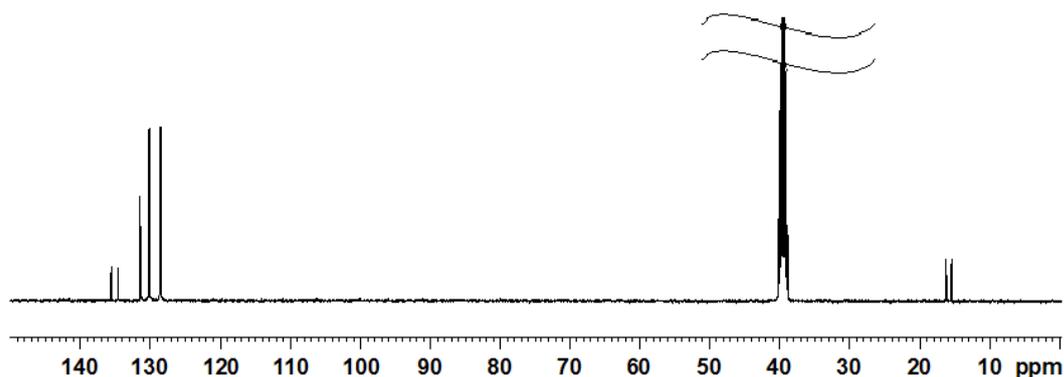


Figure S5. ^{13}C spectrum of biphenyl methyl phosphine oxide in DMSO-d₆.

2^ostep: preparation of bis (3-nitrophenyl) methyl phosphine oxide 3

The biphenyl methyl phosphine oxide **2** (5 g, 0.023 mol) was charged into a 100 ml two necked round bottom flask equipped with a magnetic stirrer, a reflux condenser and an addition funnel. The flask was placed in an ice bath and concentrated sulfuric acid (14.6 ml) was added. The mixture was stirred until the starting material dissolved. In a separate ice bath was placed a two necked round bottom flask containing nitric acid (4.31g), and sulfuric acid (9.8 ml) was introduced dropwise. The total amount of sulfuric acid was ten times by weight the weight of nitric acid, which in turn was 5% excess of the stoichiometric amount. The acid mixture was then transferred into the additional funnel and it was added dropwise to the reaction mixture, which start to become slight yellow. The reaction was allowed to continue for two hours taking care to keep temperature into a range of 0-5°C, then it was left to room temperature for another 3 hours. After this time the reaction mixture was poured in a beaker containing ice, obtaining a fluorescent yellow precipitate, which was filtered and washed several times with water until it became neutral. The product was washed with ethanol and then the solvent residual was eliminated undervacuum. The obtained powder appeared white, but when it was dissolved in DMSO-d₆ it became green. The yield was 85%.

^1H NMR (400 MHz, DMSO-d₆, ppm): δ :8.62-8.59 (2H), 8.47-8.39(2H);8.34-8.19 (2H), 7.87-7.82 (2H), 2,50-2.28 (d, 3H);

^{31}P NMR (161.97 MHz, DMSO-d₆, ppm) shown a single peak (32.28 ppm);

^{13}C (400 MHz, DMSO-d₆, ppm): d:147.8 (s) 137.1-135.8 (d, J(C,P)) ; 136.6 (s), 130.7 (s), 126,7 (s), 124,9 (s), 15.71-14.73

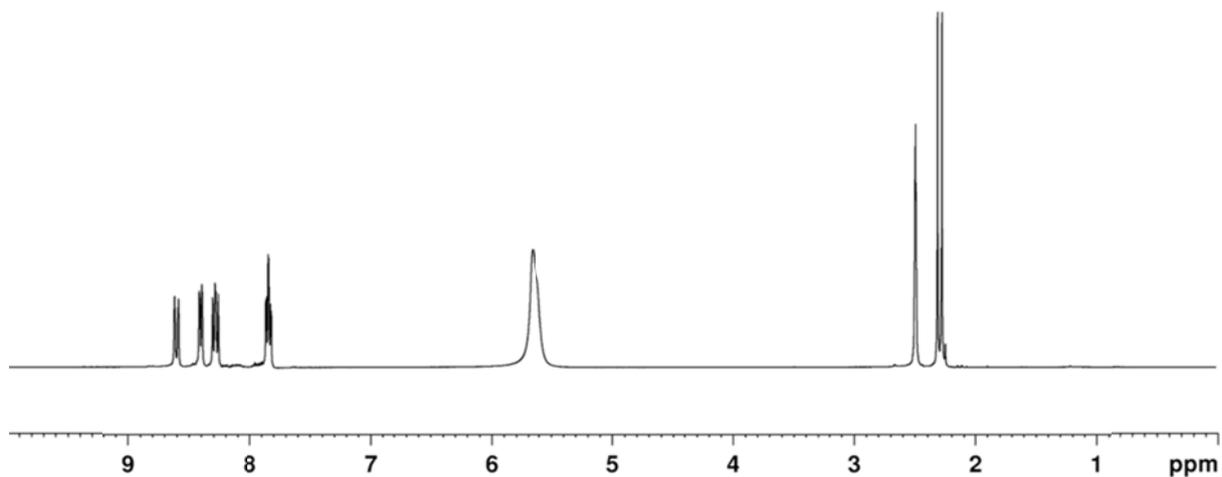


Figure S6. ^1H spectrum of binitro phenyl methyl phosphine oxide in DMSO-d6.

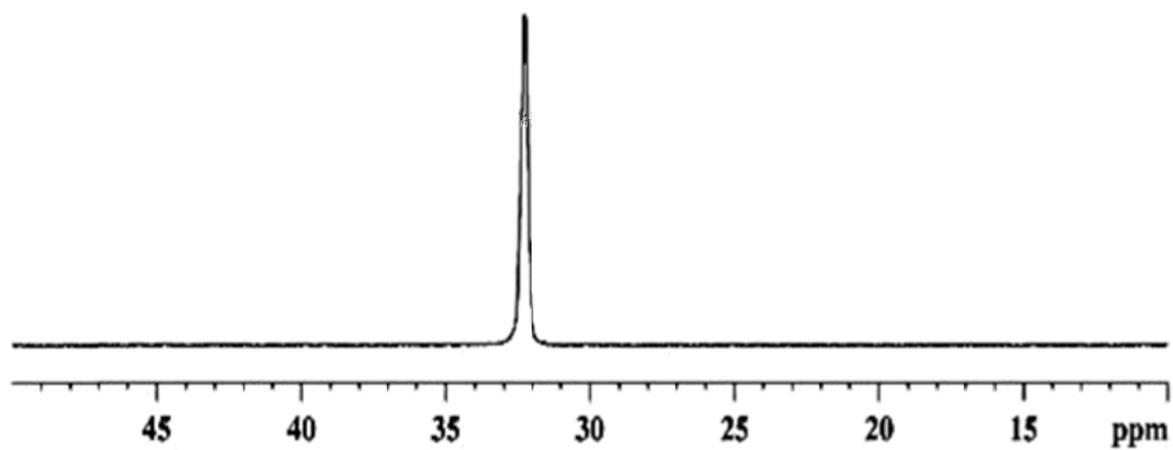


Figure S7. ^{31}P spectrum of binitro phenyl methyl phosphine oxide in DMSO-d6.

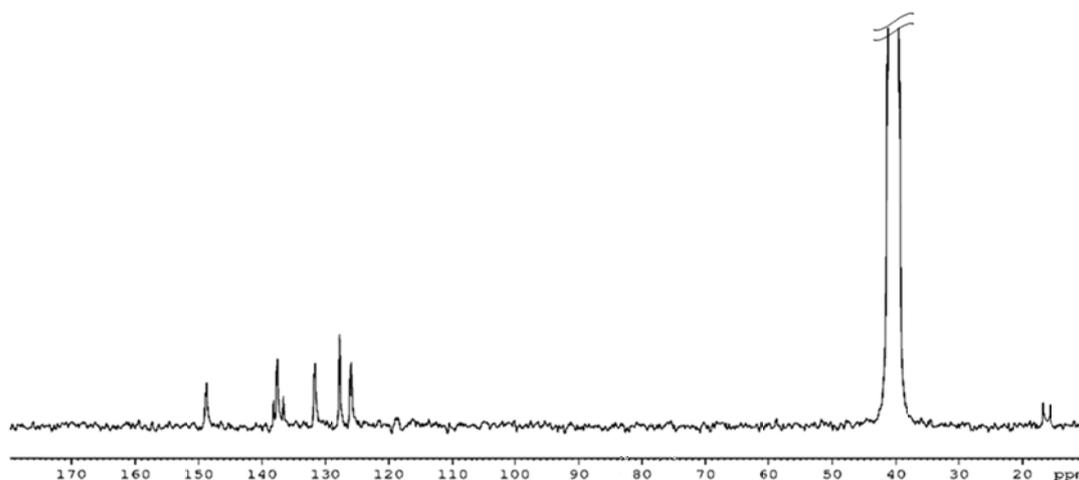


Figure S8. ^{13}C spectrum of binitro phenyl methyl phosphine oxide in DMSO-d_6 .

3^ostep :preparation of bis(3-aminophenyl)methyl phosphine oxide 4 (BAMPO)

Bis(3-nitrophenyl) methyl phosphine oxide **3** (6.09 g, 0.0198 mole) was charged in a three-necked round bottom flask, equipped with an overhead stirrer, an addition funnel and a reflux condenser, and 61 mL of absolute ethanol was added, heating the mixture at 50 °C until the starting material dissolved (~30 minutes). The mixture was purged with nitrogen. A small amounts of catalyst Pd/C (0.0345g) was added and hydrazine monohydrate (10.35g, 0.207 mol) was added dropwise from the addition funnel. This reaction step did not require heating since the reaction is exothermic. During the evolution of the reaction were observed several changing in the color of the mixture. From yellow to dark green to black, furthermore the evolution of gas from the mixture denoted that the reaction was occurring. When the reaction slowed down as indicated by a slowing of gas evolution, a second portion of Pd/C (0.0345g) was added and the reaction was heated to reflux for three hour at 100°C, the completion of the reduction was determined by ^1H spectra. After then discoloring activated carbon (0.1g) was added to the mixture and the reaction was left to reflux for an hour. The black solution was then cooled and filtered through celite on a filter funnel with drip-tip. A yellow solution was obtained; the solvent was evaporated under vacuum and the product **4** was obtained with a yield of 72%.

The amount of catalyst used in this synthesis was slightly higher than the one suggested by Zhuang [1]; in fact, using that amount we have obtained a red oily residue that when treated with high temperature-time treatment gave a viscous residue, which was insoluble in the majority of solvents. As suggested by Bilow et al. [2], an equi-volume hexane-benzene mixture was added to this residue but it was not possible to separate the desired product. Separation on silica gel using a mixture of chloroform and methanol (9:1) was successful, but gave very low yields (lower than 35% of recovered product). The best solution was found in adding chloroform to the red oily liquid residue. The red oil solution was not soluble in chloroform, whereas solvent resulted yellow. A separator funnel was used and the solution was filtered several times. Solvent was then evaporated under vacuum, with a yield of 65%.

^1H , ^{31}P , and ^{13}C spectra of bis(3-aminophenyl) methyl phosphine oxide are reported in FigureS9-S10-S11 respectively.

^1H NMR (400 MHz, DMSO-d_6 , ppm): d: 6.647.13-7.06 (2H); 6.89-6.64 (6H) 5.3 (s, 4H), 1.79(d, 3H);

^{31}P NMR (161.97 MHz, DMSO-d_6 , ppm) shown a single peak (33.6 ppm),

^{13}C 100 MHz, DMSO-d_6 , ppm): d :148.7-148,6 (d,J(C,P)129.1-128.9,-117.01-116.4, 115.1-115.0, 16.3,15.6 (d, J(C,P)

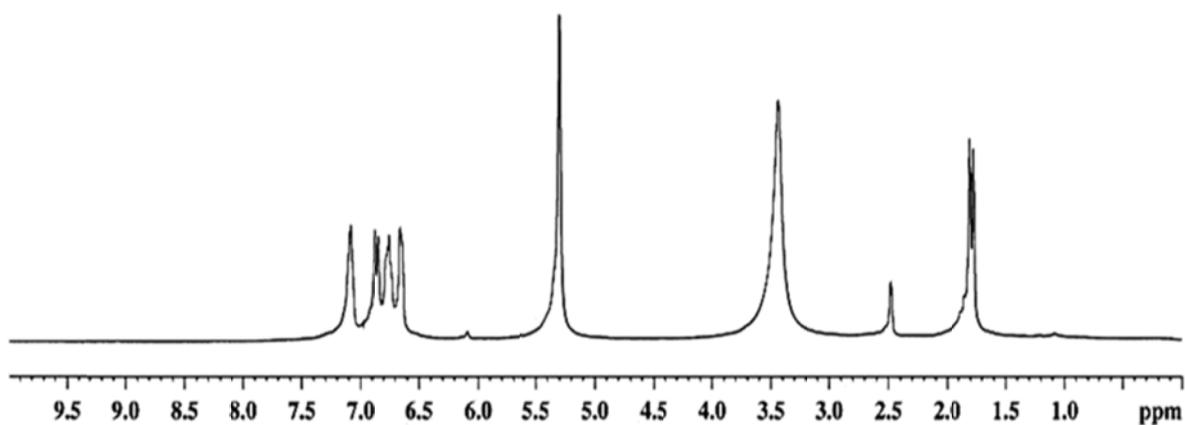


Figure S9. ¹H spectrum of bis(3-aminophenyl) methyl phosphine oxide 4 (BAMPO) in DMSO-d₆.

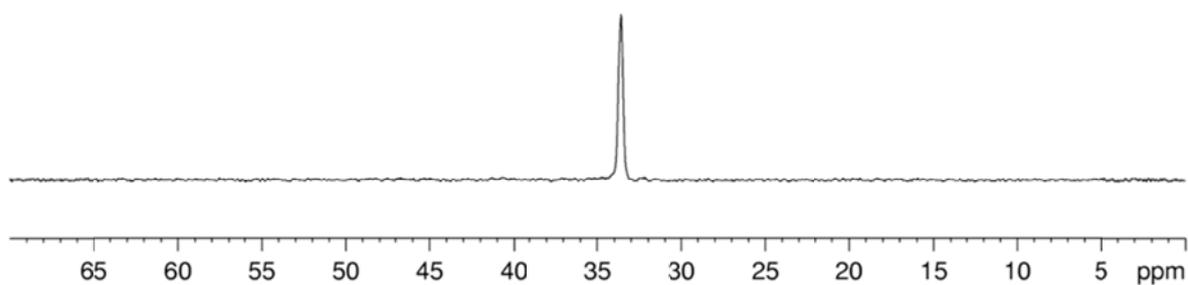


Figure S10. ³¹P spectrum of bis(3-aminophenyl) methyl phosphine oxide 4 (BAMPO) in DMSO-d₆.

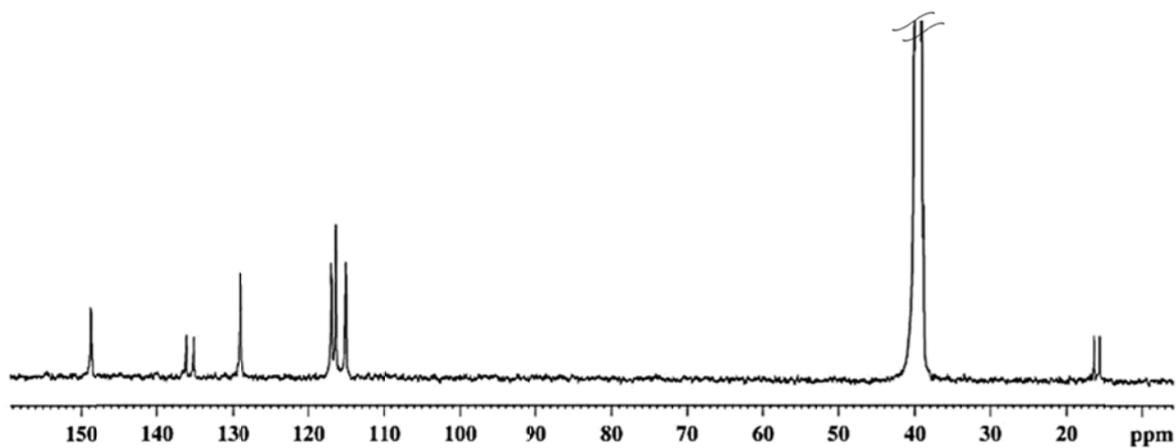


Figure S11. ¹³C spectrum of bis(3-aminophenyl) methyl phosphine oxide 4 (BAMPO) in DMSO-d₆.

Synthesis of bis(3-aminophenyl) phenyl phosphine oxide (BAPPO)

In this section we describe the synthesis procedure of bis(3-aminophenyl) phenyl phosphine oxide as flame retardant containing phosphorous to be used in epoxy resins for aeronautic applications.

Bis(3-aminophenyl) phenyl phosphine oxide **3** (BAPPO) was synthesized via a two-step route. Firstly, the bis(3-nitrophenyl) phenyl phosphine oxide **2** was obtained as an intermediate following the procedure suggested by Liu et al.[3]. Then BAPPO was obtained by reduction of the intermediate by means of hydrazine monohydrate following the procedure suggested by Zhuang [1] with slight modifications.

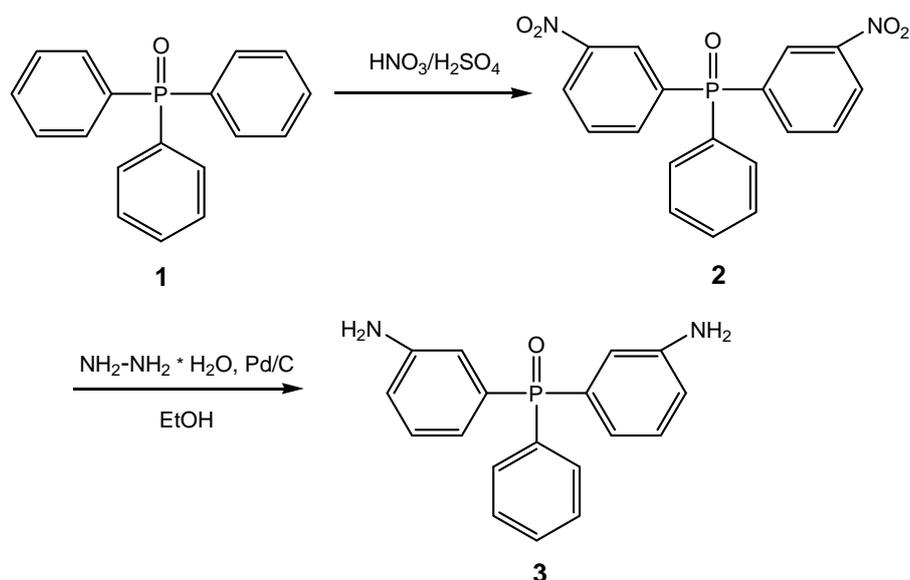


Figure S22. Scheme of synthesis of bis(3-aminophenyl) phenyl phosphine oxide **3**.

1st step: preparation of bis(3-nitrophenyl) phenyl phosphine oxide **2**

Triphenyl phosphine oxide **1** (5 g, 0.018 mol) was charged into a 250 ml two necked round bottom flask equipped with a magnetic stirrer and a reflux condenser, then 36 ml of sulphuric acid were added. In a salt/ice bath was placed a two necked round bottom flask containing nitric acid (2.61g), and sulfuric acid (18 ml) was introduced dropwise. The amount of nitric acid that is required must be carefully controlled in order to obtain a high yield of the dinitro compound. The acid mixture was then transferred into the addition funnel and it was added dropwise to the reaction mixture over a period of 2 hours, taking care to keep the temperature in a range of [-5;0]°C, then it was left to room temperature overnight. After this time, the reaction mixture was poured in a beaker containing ice, obtaining a fluorescent yellow precipitate. After the ice melted, the mixture was extracted with chloroform and washed with a sodium bicarbonate aqueous solution until neutral pH. The solvent was removed under vacuum obtaining a viscous residuum, then EtOH was added. This caused the obtainment of a precipitate. The soluble fraction was recovered from the mixture and the solvent was removed under vacuum. A white powder was obtained, which became green when dissolved in deuterated DMSO-d₆.

In Figure S13 the scheme of synthesis of bis(3-nitrophenyl) phenyl phosphine oxide **2** is shown.

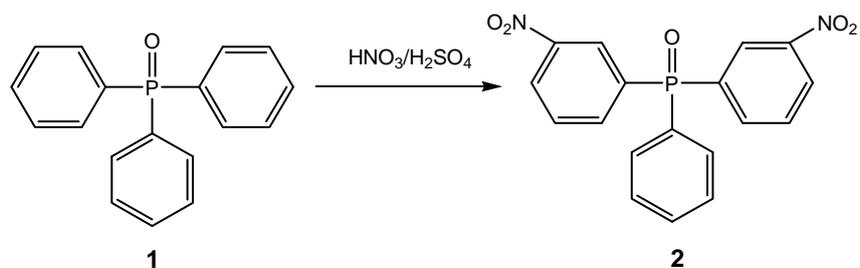


Figure S13. Scheme of synthesis of bis (3-nitrophenyl) phenyl phosphine oxide 2.

^1H , ^{31}P , ^{13}C NMR spectra confirmed the structure of **2** (Figures S14-S15-S16). The yield was 60%.

^1H NMR (400 MHz, DMSO- d_6 , ppm): δ :8.50-8.48 (2H), 8.43-8.40(2H); 8.15-8.10(2H), 7.90-7.85 (2H), 7.76-7.70 (3H), 7.64-7.59 (2H);

^{31}P NMR (161.97 MHz, DMSO- d_6 , ppm) shown a single peak (28.7 ppm);

^{13}C (100 MHz, DMSO- d_6 , ppm):147.8, 137.6; 134.4, 133.1; 131.5, 131, 129.2, 127.2; 126.0.

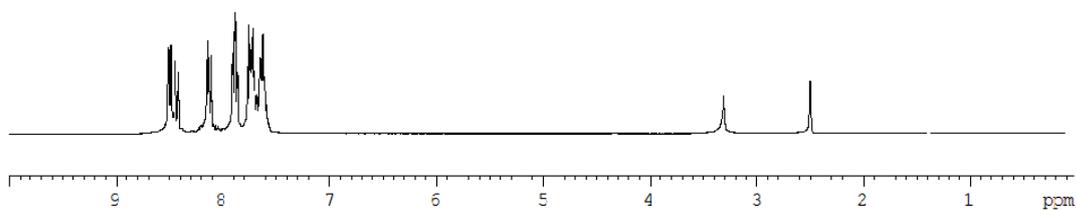


Figure S14. ^1H spectrum of bis(3-nitrophenyl) phenyl phosphine oxide 2 in DMSO- d_6 .

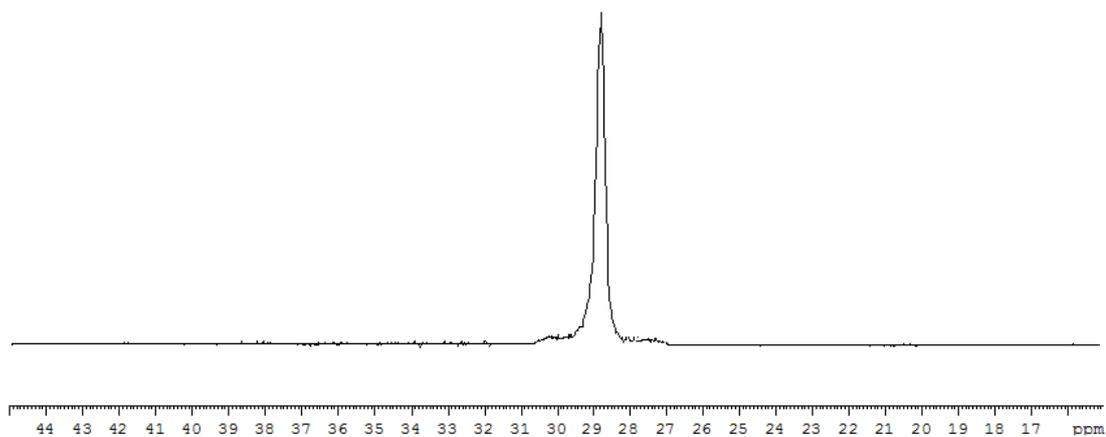


Figure S15. ^{31}P spectrum of bis(3-nitrophenyl) phenyl phosphine oxide 2 in DMSO- d_6 .

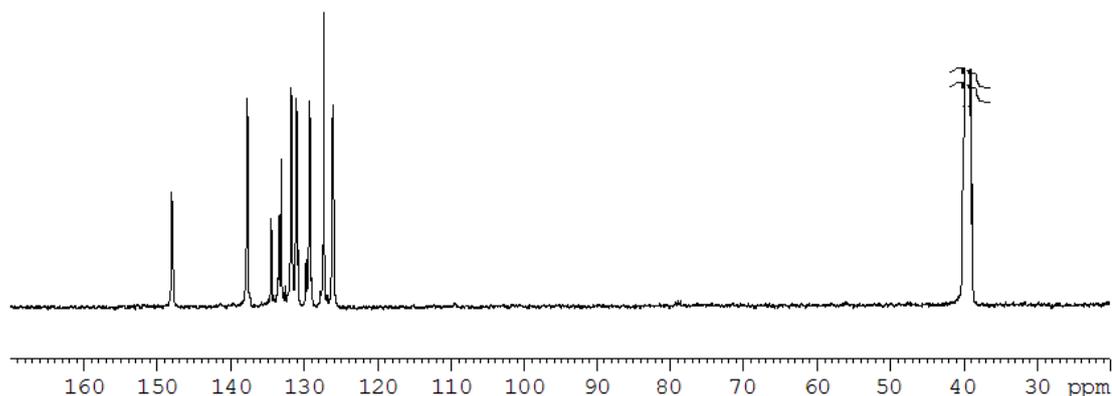


Figure S16. ^{13}C spectrum of bis(3-nitrophenyl) phenyl phosphine oxide **2** in DMSO- d_6 .

2^ostep :preparation of bis(3-aminophenyl) phenyl phosphine oxide 3 (BAPPO)

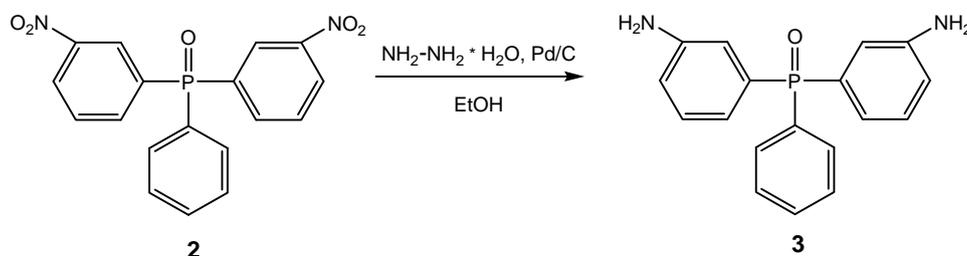


Figure S17. Scheme of synthesis bis(3-aminophenyl) phenyl phosphine oxide **3** (BAPPO).

Bis(3-nitrophenyl) phenyl phosphine oxide **2** (6.09 g, 0.0198 mole) was charged in a three-necked round bottom flask, equipped with an overhead stirrer, an addition funnel and a reflux condenser, then 61 mL of absolute ethanol was added, heating the mixture at 50 °C until **2** was dissolved (~30 minutes). The mixture was purged with nitrogen. A small amount of catalyst Pd/C (0.0345g) was added and hydrazine monohydrate (10.35 g, 0.207 mol) was added dropwise by the addition funnel. This reaction step did not require heating since the reaction is exothermic. During the evolution of the reaction several changing in the color of the mixture were observed, from yellow to dark green to black. When the reaction slowed down as indicated by a slowing of gas evolution, a second portion of Pd/C (0.0345g) was added and the reaction was heated to reflux for 4 hours at 100°C, the completion of the reduction was determined by NMR ^1H spectrum, after discoloring activated carbon (0.1g) was added to the mixture and the reaction was left to reflux for one hour. The black solution was then cooled and filtered through celite on a filter funnel with drip-tip. A yellow solution was obtained; the solvent was evaporated under vacuum and the product **3** was obtained with a yield of 75%.

^1H , ^{31}P , and ^{13}C spectra of bis(3-aminophenyl) phenyl phosphine oxide are reported in Figures S18-S19-S20, respectively.

^1H NMR (400 MHz, DMSO- d_6 , ppm): 7.60-7.52 (5H); 7.15-7.11 (2H) 6.86-6.59 (6H) 5.39 (4H), 1.79(d, 3H);

^{31}P NMR (161.97 MHz, DMSO- d_6 , ppm) shown a single peak (32.2 ppm) ;

^{13}C 100 MHz, DMSO- d_6 , ppm):149.1, 134.5, 133.1, 131.8, 129.3, 128.6, 118.9, 117.2,116.6.

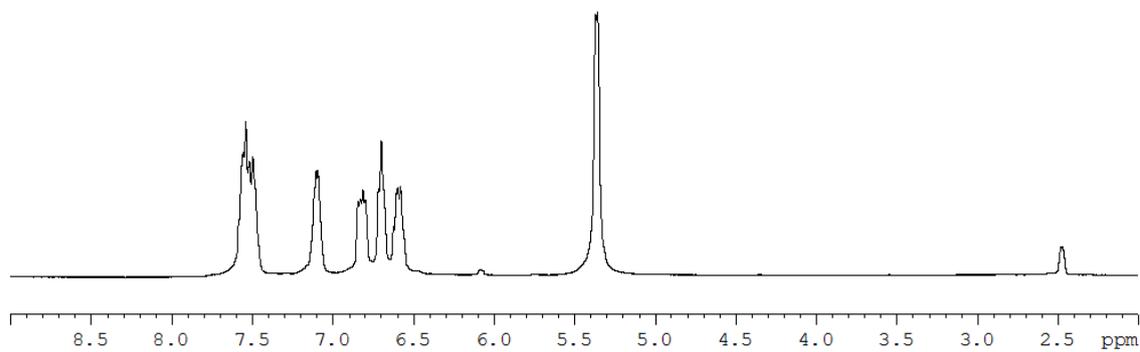


Figure S18. ¹H spectrum of bis(3-aminophenyl) phenyl phosphine oxide 3 (BAPPO) in DMSO-d₆.

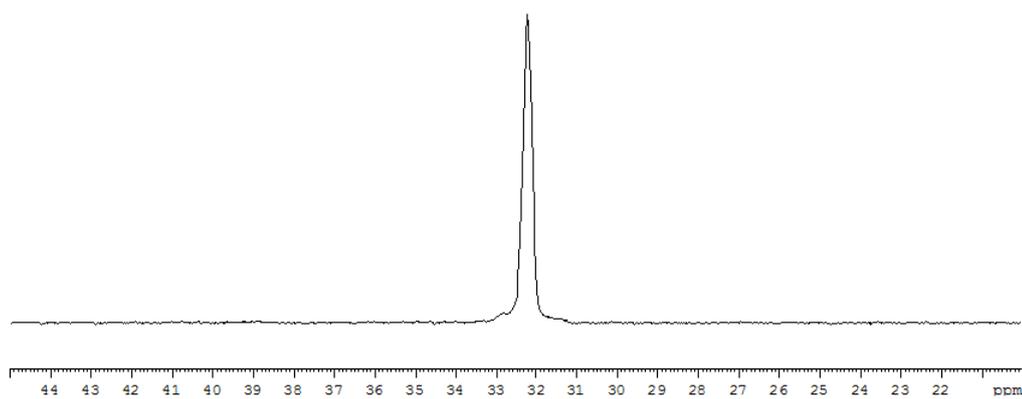


Figure S19. ³¹P spectrum of bis(3-aminophenyl) phenyl phosphine oxide 3 (BAPPO) in DMSO-d₆.

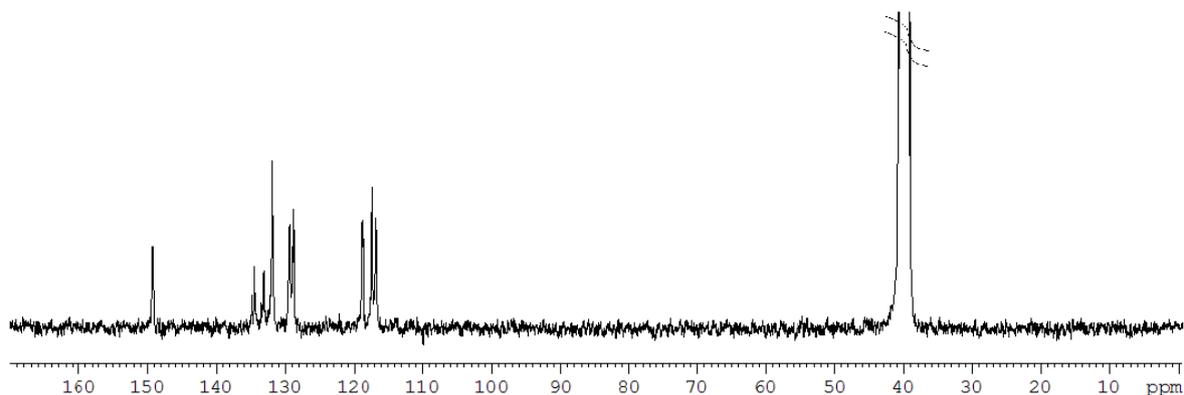


Figure S20. ^{13}C spectrum of bis(3-aminophenyl) phenyl phosphine oxide 3 (BAPPO) in DMSO-d_6 .

FTIR Investigation

Chemical structures of the synthesized organophosphorus compounds was characterized by FTIR spectroscopy.

FTIR spectra of BAMPO and BAPPO are depicted in Figure S21. The formation of aromatic primary amine groups in these molecules is confirmed by IR absorption peaks in the range of values of about $3462\text{--}3220\text{ cm}^{-1}$ (N-H stretching vibration). Other peaks at 1172 and 1157 cm^{-1} (P=O group in the BAPPO and BAMPO spectra respectively) and 1437 and 1442 cm^{-1} (P-Ph group in the BAPPO and BAMPO spectra respectively) confirm the presence of phosphine oxide moiety in these compounds.

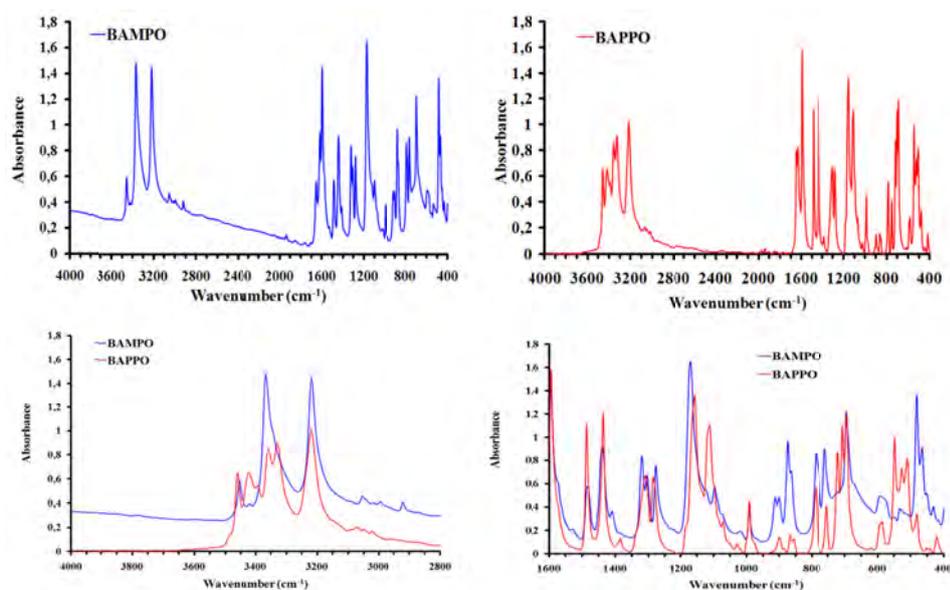


Figure S21. FTIR spectra of BAMPO and BAPPO.

References

- [1] H. Zhuang. Synthesis and characterization of aryl phosphine oxide containing thermoplastic polyimides and thermosetting polyimides with controlled reactivity. *Ph.D. Thesis*, Virginia Polytechnic Institute And State University, 1998
- [2] N. Bilow, T. W. Giants, R. K. Jenkins, P. L. Campbell. Development of phosphorylated adhesives. *NASA Technical Report* 1983, (Document ID: 19830023453), United States.
- [3] Y. L. Liu, G. H. Hsiue, R. H. Lee, Y. S. Chiu. Phosphorus-containing epoxy for flame retardant. III: Using phosphorylated diamines as curing agents. *J. Appl. Polym. Sci.*, 1997, 63, 895-901.