

Extension of the Self-Consistent Spectrophotometric Basicity Scale in Acetonitrile to Full Span of 28 pK_a Units: Unification of Different Basicity Scales

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Supporting Information

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Chemicals, Purification and Characterization of Compounds

Chemicals. Compounds **1 - 7, 8 - 37, 40 - 45, 47 - 67, 69, 71, 72, 74, 75, 81, 83, 88, 89** were the same as used earlier.^{1,2,3,4,5,6} 5-Nitrobenzimidazole (**68**) (98%), Methyldiphenylphosphine (**70**) (99%), 2,4-Difluoroaniline (**76**) (99%), 4-Nitroaniline (**84**) (“pure for analysis”) were used without additional purification. 1-Naphtylamine (**73**) (“pure for analysis”) sublimed under atmospheric pressure under dried argon and was kept in dessicator over KOH. 4-(trifluoromethyl)-aniline (**77**) (99%) was distilled from CaH₂ under reduced pressure. 2-Chloroaniline (**78**) ($\geq 98\%$) was distilled fractionally from CaH₂ under reduced pressure. 3-Nitroaniline (**79**) (“pure”) was recrystallized once from ethanol and then from ethanol and water mixture, washed and solvent traces were removed by rotational evaporator and substance was kept in desiccator over KOH. 4-Pyrrolidinopyridine (**39**) (98%), 2-Aminoacridine (“pure”) (**46**), 3-Nitro-4-fluoroaniline (**80**) (97%), Triphenylphosphine (**82**) (97%), 2,5-Dichloroaniline (**85**) (99% (GC)), Diphenylamine (**86**) (“pure”), 2,6-Dichloroaniline (**88**) (98%) were recrystallized from ethanol, crystals were washed with ethanol and solvent traces were removed under vacuum and substances were kept in vials in desiccator over KOH.

Experimental setup

Experimental setup. The spectrophotometric titration method used in this work is mostly the same as described earlier^{6,5,2} i.e., the simultaneous titration of two free bases with an acid of comparable basicity was carried out and the UV-Vis spectra was recorded after each addition of acidic titrant. Also, both bases were titrated separately. Professional glovebox was used to ensure that the environment is free from the humidity and oxygen. Glassware used during the experiments was heated at 150 °C for at least six hours and then cooled in desiccator over P₂O₅. The UV-Vis measurements were carried out in

an external cell compartment, situated in the glovebox. The cell compartment was connected to the UV-Vis spectrophotometer by means of two quartz fiber optic cables. Concentrations of bases were during the titration experiments in 10^{-5} M range. Solutions made from strong ($pK_a > 24$) free bases were protonated up to ten percent; strongest bases ($pK_a > 30$) were protonated up to several tens of percent. This means that solvent contains less than 4×10^{-6} M some acidic impurities (acetic acid etc) with pK_a around 24 units and less than 2×10^{-5} M acidic impurities with pK_a around 30 - 31 units. Before a titration experiment, i.e. the titrating the solution containing the two bases with an acid, the formed conjugate acids of strong bases were neutralized by adding solution of a stronger alkyl P₁ or P₂ phosphazene base. This way it was ensured that both bases were entirely in the deprotonated form. The temperature inside the glovebox and external sample compartment was monitored with the thermometer and adjusted by cooling the ambient room temperature or warming the box atmosphere with electric lamp. Generally the temperature was 25 – 26 °C and it never exceeded the 24 – 28 °C limits.

The titrant solution of the EtP₂(dma) base in AN was found not to be fully stable under our experimental conditions. After a few hours standing a small amount of a compound, having maximum absorbance at 258 nm in strongly basic solution formed in the solution. This compound can be the 4-amino-2,6-dimethylpyrimidine⁷ or some other AN condensation product. No attempt was made to isolate or identify this unknown compound as its concentration was very low in fresh EtP₂(dma) solution and it did not really interfere with the measurements.

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Figure S1. ^{13}C -NMR spectra of selected compounds

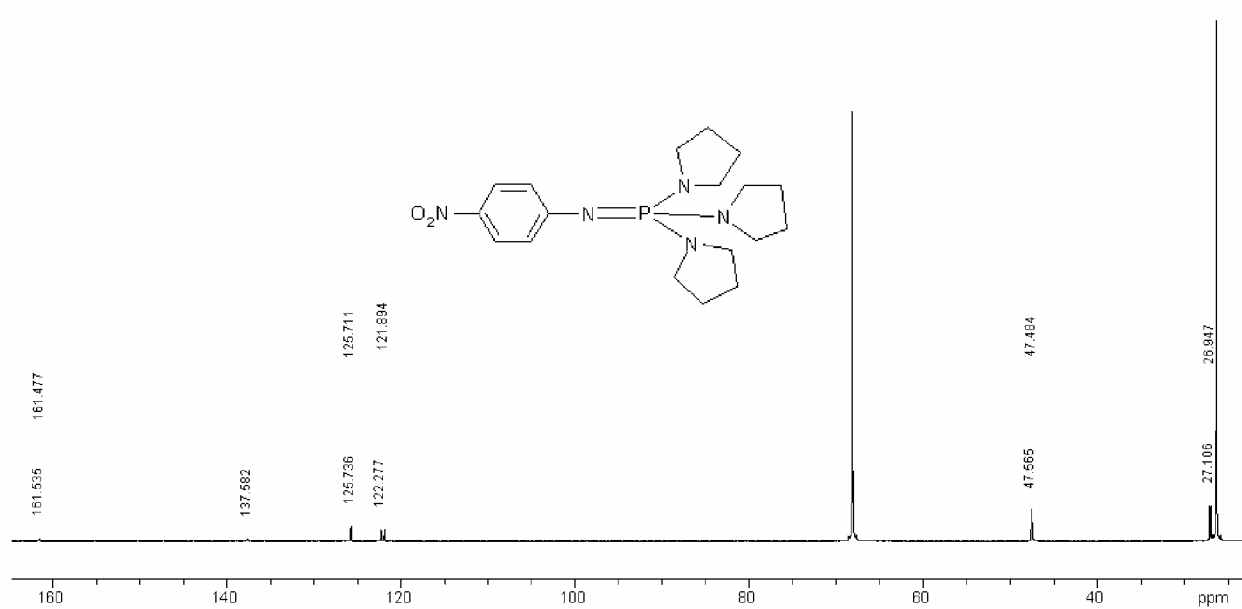


Figure S1-1. 4-NO₂-C₆H₄P₁(pyrr) (**38**).