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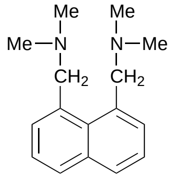
Protonation of Very Strong Bases by Phenols in Non-aqueous Solutions

Bogumił Brzeziński,[a] Eugeniusz Grech,[b] Zbigniew Malarski,[c] Maria Rospenk,[c] Grzegorz Schroeder[a] and Lucjan Sobczyk*[c]

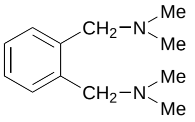
[a]*Faculty of Chemistry, A. Mickiewicz University, 60-780 Poznań, Poland*
[b]*Institute of Fundamental Chemistry, Technical University, 71-065 Szczecin, Poland*
[c]*Faculty of Chemistry, University of Wrocław, 50-383 Wrocław, Poland*

The interactions between the very strong proton sponge bases 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) and Phosphazene Base, P_2Et, and phenols of varying strength were studied in non-aqueous solutions using UV–VIS and IR spectroscopy.

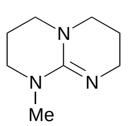
Whilst the interaction of proton sponges **1** and **2** with various proton donors has been the subject of numerous studies,[8] there is little known about the complexation of very strong bases **3** and **4** in non-aqueous solvents.[14] Consequently IR and UV–VIS studies of these bases with phenols were undertaken. Phenols can be considered as model proton donors[15] as, by the introducing of various substituents, one can regulate their acidity over a broad pK_a range. Their UV spectra are a sensitive indicator of the interaction strength and particularly of the degree of proton transfer. On the other hand, the IR spectra of the phenol complexes with bases provide important information on the features of hydrogen bonds formed between OH groups and the basic centres. 4-Methylphenol, 4-chlorophenol, 4-cyanophenol, 2,4,6-trichlorophenol and pentachlorophenol were used in CCl_4, $CHCl_3$, CH_2Cl_2 and MeCN. A variety of situations were found to be present depending on the solvent and phenol used. For weaker phenols in non-polar CCl_4 complexation equilibria without proton transfer were observed whereas in the case of stronger phenols in MeCN complete complexation and the creation of strongly polar[8] proton transfer states take place. Various intermediate states were found for medium strong phenols in weakly polar solvents. In many cases the ion pairs are characterized by extended charge separation. The UV band shifts upwards very long wave lengths, Fig. 1.



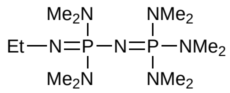
1 DMAMN



2 DMAMB



3 MTBD



4 P_2Et

The IR spectra reflect the complicated situation which appears in the intermediate states, Fig. 2. For 1:1 complexes only a weak band assigned to the 'free' N^+–H group occurs which is characteristic of a tetrachloroaureate salt and a 'continuum' characteristic of hydrogen bridges with double minimum or with a broad asymmetrical single minimum potential.[18] For the 2:1 complexes the intensity of the continuum reaches high values that correspond to the formation of $(OHO)^-$ bridges. Simultaneously the intensity of the ^+N–H bands indicates a full proton transfer to the MTBD molecule.

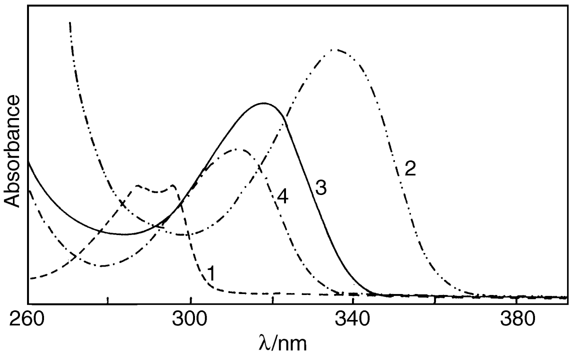


Fig. 1 UV spectra of 2,4,6-trichlorophenol–MTBD systems in MeCN: (1) phenol; (2) 1:1 system; (3) phenol in CCl_4 with added KOH in ethanol; (4) phenol in water with KOH

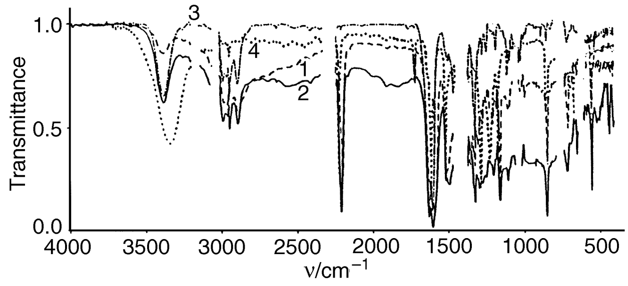


Fig. 2 IR spectra of 4-cyanophenol–MTBD systems in MeCN: (1) 1:1 system; (2) 2:1 system; (3) $MTBD{\cdot}HAuCl_4$ salt; (4) phenol

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Techniques used: IR, UV–VIS
References: 31
Table 1: pK_a values of N-bases in acetonitrile
Table 2: Complexation and proton transfer equilibrium constants for systems phenols-strong bases in various solvents with positions of phenolic band in the UV region
Figs. 1–9: UV and IR spectra of various phenol-N-base systems in non-aqueous solvents

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References cited in this synopsis

8 B. Brzeziński, A. Jarczewski, J. Olejnik and G. Schroeder, *J. Chem. Soc., Perkin Trans. 2*, 1992, 2257; G. Schroeder, B. Brzeziński and A. Jarczewski, *J. Mol. Struct.*, 1992, **274**, 83; G. Schroeder, B. Brzeziński, Z. Malarski and L. Sobczyk, *Pol. J. Chem.*, 1994, **68**, 261.
14 B. Brzeziński, P. Radzijewski and G. Zundel, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 3141.
15 Th. Zeegers-Huyskens and P. Huyskens, *Proton Transfer and Ion Transfer Complexes in Molecular Interactions*, eds. H. Ratajczak and W. J. Orville-Thomas, Wiley, New York, 1980, vol. 2.
18 G. Zundel, *Trends Phys. Chem.*, 1992, **3**, 129.

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*To receive any correspondence.