The Nature of the HB. 2. Predicting HB Strength by the pKa Slide Rule

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All HBs between neutral molecules are to be considered acid-base equilibria, R-D-H---:A-R \Leftrightarrow R-D⁻---H-A⁺-R, and their strength is determined by the difference $\Delta pK_a = pK_{AH}(R-D-H) - pK_{BH}(R-A-H^+)$, the HB becoming the stronger the smaller $\Delta p K_a$ is. In fact, the limit $\Delta p K_a = 0$ corresponds to the condition by which the proton is equally shared by the two groups so that the HB is transformed from a weak electrostatic interaction into a strong proton-centred 3-centre-4-electron R-D^{1/2---} A-R covalent bond. The *a priori* appraisal of $\Delta p K_a$ is therefore a promising method for predicting HB strengths among organic compounds provided the pK_a values of the interacting molecules are known. This communication presents for the first time detailed lists of pK_{AH} and pK_{BH} values covering most classes of organic compounds and arranges them in an unique chart, called the pK_a slide rule, that makes it possible to predict the approximate strength of the HBs formed by any couple of organic HB donors and acceptors by simple inspection. Previsions obtained through the pK_a slide rule are compared with the results of diffraction experiments through an extensive search of all reasonably accurate R-O-H---:NR3 \Leftrightarrow R-O⁻---H-N⁺R₃ HBs present in the CSD and subdivided in chemical groups (10 of donors and 14 of acceptors). It is shown that many HBs are intrinsically weak because of impossible pK_{AH}/pK_{BH} matching and that strong HBs can be obtained only by combining donor and acceptor molecules for which the $\Delta p K_a \approx 0$ condition is actually accessible.

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