Photoacids. Ground and excited state acidities of 2-naphthol and its cyano derivatives

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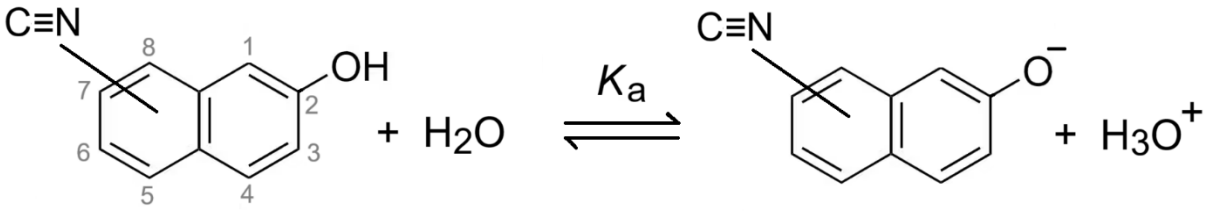

ABSTRACT.

The ground and excited state acidities of 2-naphthol and five of its cyano derivatives are investigated by theoretical methods, applying the semiempirical *W* parameter and electric potentials computed with HF (Hartree-Fock) and CIS (Configuration Interaction Singles) theory. The measured acidity exponents are found to correlate with the potentials computed for the oxygen atoms in the conjugate bases, the 2-naphtholate anions. The computed potentials account adequately for the relative acidities; the excited state acidity exponents (pK_a*) determined by the Förster cycle are thus predicted with a SD (Standard Deviation) of 0.3 pK_a unit. Intramolecular two-center contributions are found to be of importance for the quality of the correlation. The calculated potentials predict that cyano-substitution in the positions 3, 5, and 7 are particularly effective in enhancing the photoacidity. The 5,7-dicyano derivative is thus predicted to be a stronger photoacid than the 5,8-dicyano derivative.

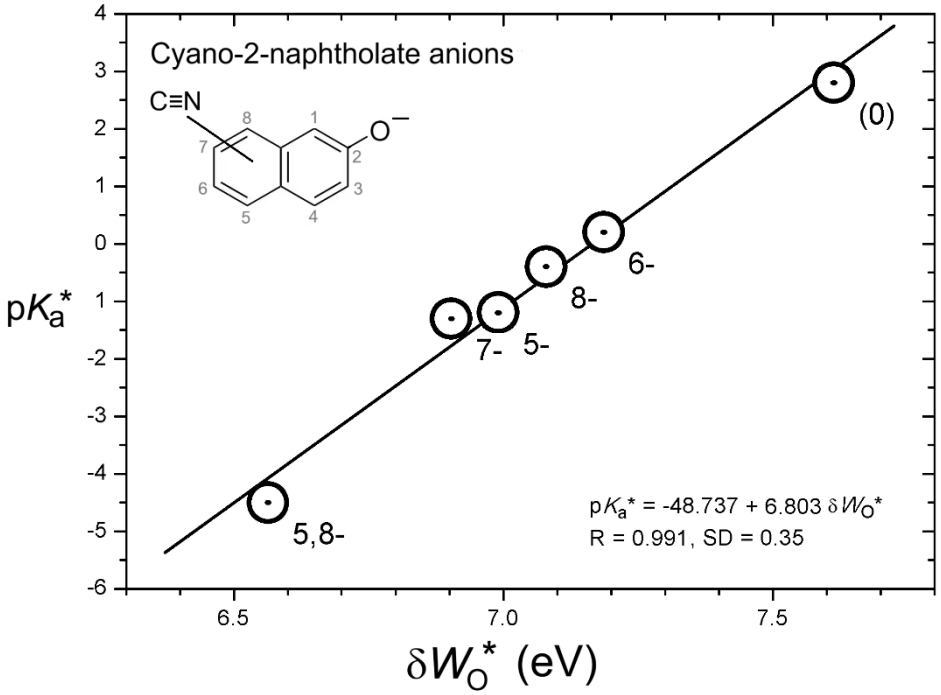

Figure 3. Excited states: Linear regression of observed acidity exponents pK_a* (Table 1, Förster values) on calculated δW_O* parameters for the 2-naphtholate anion and its cyano derivatives (Table 2, vertical excitations).

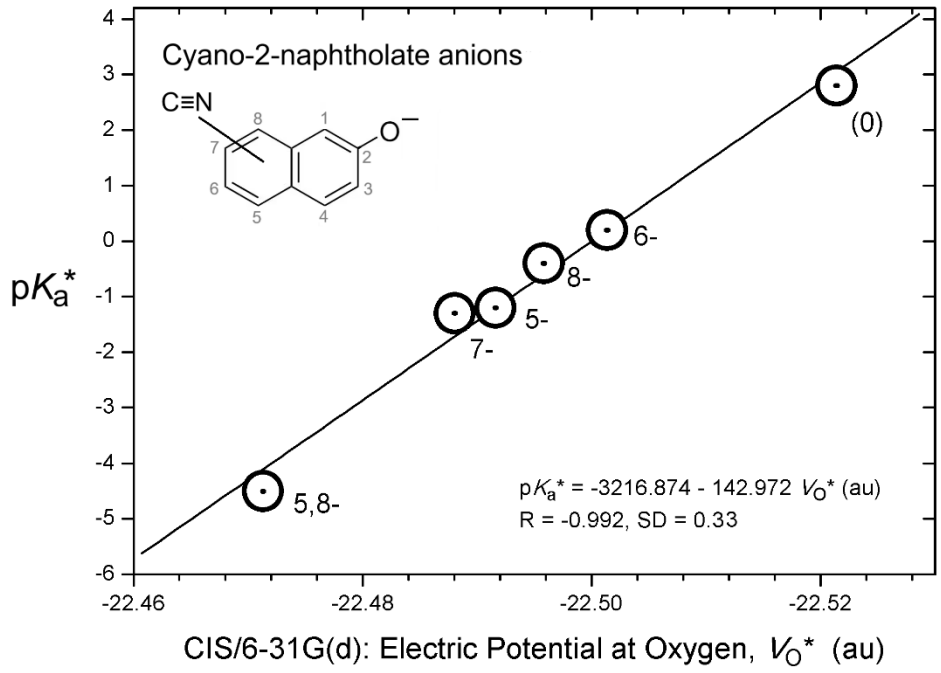

Figure 4. Excited states: Linear regression of observed acidity exponents pK_a* (Table 1, Förster values) on calculated V_O* electric potentials for the 2-naphtholate anion and its cyano derivatives (Table 3).