

Computational Study of Substituent Effects on Gas-Phase Stabilities of Phenide Anions

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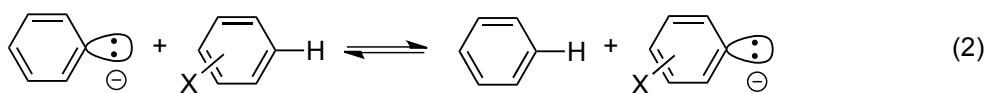
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Stabilities of anions of aromatic compounds are governed by three kinds of electronic effects, and an extended Yukawa-Tsuno equation (1) was recently proposed to describe the substituent effects.¹

$$-\Delta E_X = \rho(\sigma^0 + r^-\Delta\bar{\sigma}_R + s\Delta\bar{\sigma}_S) \quad (1)$$

In order to establish the generality of Eq. 1 and reveal the physical meanings of resultant constants (the r^- and s values), more extensive analyses on various anionic species are desirable. Here, we extended the research to phenide anions. The relative stabilities of ring-substituted phenide anions were determined as energy differences (ΔE_X) of proton transfer reactions (2).



Energies of respective species were calculated by DFT method. Obtained substituent effects were analyzed by Eq. 1 to give an extended Yukawa-Tsuno plot as shown in Fig. 1. The r^- value of 0.0 and the s value of 1.1 were obtained, showing the absence of the through-resonance and the significance of the saturation effect, respectively. This can be interpreted by the structure of phenide anion in which the anionic p-orbital is attached directly to the *ipso* position of the benzene ring but is orthogonal to the benzene π -electron system. The independent relation between the r^- and s values in various carbanions revealed that two kinds of electronic effects quantified by the r^- and s values are independent with each other showing adequacy of Eq. 1.

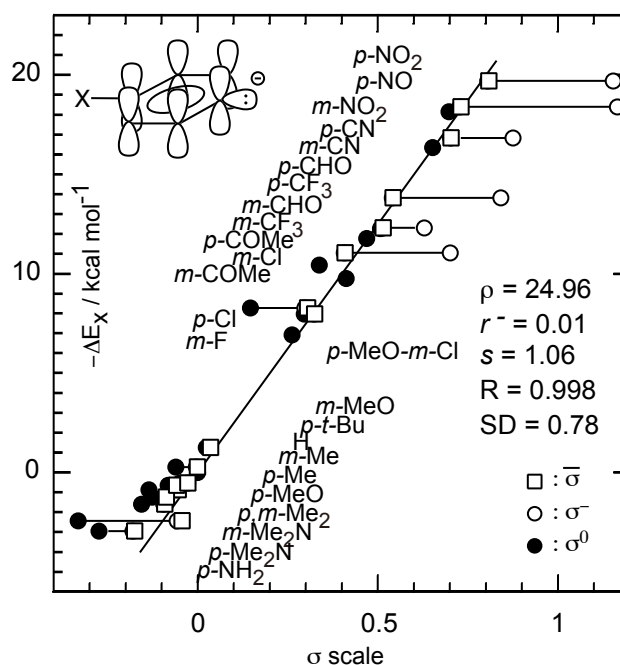


Fig. 1. Extended (Y-T) plots of $-\Delta E_X$ of phenide anions.