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COMPUTATIONAL STUDY OF SUBSTITUENT EFFECTS ON GAS-PHASE STABILITIES OF 1-PHENYLCYCLOBUTANE-1,3-DIYLIUMS

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Yukawa-Tsuno equation ($-\Delta E_X = \rho(\sigma^0 + r^+\Delta\bar{\sigma}_R^+)$) (1) has been widely used for over a half century to analyze substituent effects on stabilities of cations of benzene derivatives, which treat the electronic effects of ring substituents dividing into two terms. The σ^0 substituent constant measures the general electronic effect. The $\Delta\bar{\sigma}_R^+$ measures the additional stabilizing capability by the through-resonance effect for *para* –R groups.

In this study, 1-phenylcyclobutane-1,3-diylium (**1**) and its analogs bringing various functional groups at position 3 were chosen, and their substituent effects on gas-phase stabilities were analyzed to reexamine eq. 1. Relative gas-phase stabilities (ΔE_X) of these ring-substituted dications were computationally determined using isodesmic reactions with substituted benzene.

In Figure 1, substituent effects of **1** were compared to those of α,α-dimethylbenzyl cations having 90°-fixed dihedral-angle between the cationic side chain and the benzene ring that have been used as a reference system of σ^0.[1] Plots of *meta* EDGs gave an excellent linear correlation. Plots of *para* –R groups deviated upward from the correlation line, showing the larger degree of the through-resonance effect in **1**. Plots of EWGs also deviated upward from the correlation line. This fact implies that the other kind of stabilizing effect is operating on these derivatives. Examinations of substituent effects of all dicationic systems revealed that the three-term extended Yukawa-Tsuno equation ($-\Delta E_X = \rho(\sigma^0 + r^+\Delta\bar{\sigma}_R^+ + s^+\Delta\bar{\sigma}_s^+)$) is necessary to analyze the substituent effects of these dications.
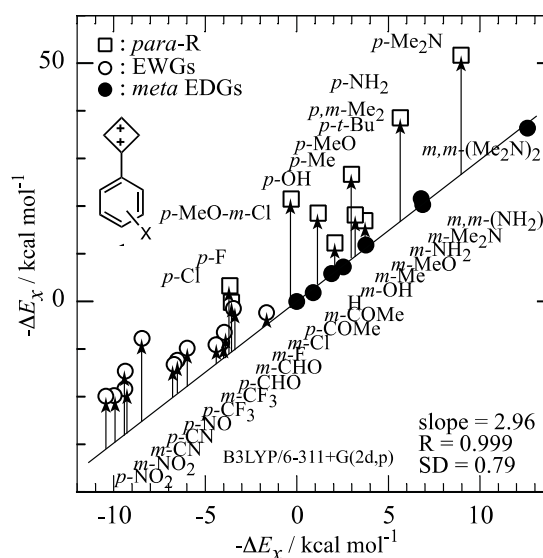

Fig. 1. Comparison of substituent effects.

REFERENCE

[1] K. Nakata, M. Fujio, K. Nishimoto, Y. Tsuno, *J. Phys. Org. Chem.* **2003**, *16*, 323–335.