

# The substituent effect in the doubly-charged benzene

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The substituent effect belongs to the one of the most important aspects of the general and the physical organic chemistry. Usually, it is considered as an effect associated with interaction between a specific chemical group (the substituent), possessing some given electron donating/withdrawing power, and the aromatic ring or other  $\pi$ -conjugated system. The interaction between the substituent and the substituted ring usually leads to important changes in various physical and chemical properties of the chemical compound. On the other hand, the substitution, although, it changes significantly, e.g. reactivity of the given aromatic ring, leads to very limited changes in the degree of  $\pi$ -electron delocalization. For instance, the substitution of the benzene ring with  $-\text{NO}$  or  $-\text{OH}$  group results in reduction of  $\pi$ -electron delocalization of the benzene ring by less than 1% (as shown by HOMA index [1]). This is due to the fact, that benzene ring, as distinct from its nonaromatic counterparts [2,3] tends to keep its aromatic character, and thus, is relatively resistant for substituent effect.

Here, we present the results of the investigation on the substituent effect in doubly positively charged benzene derivatives. The benzene dication, being  $4n$  Hückel system, seems to be much more sensitive for the substituent effect when compared with its neutral counterpart. The interaction of several various substituents, possessing different electron donating/withdrawing properties, and interacting via the substituent effect with mono- and disubstituted benzene dications in its singlet and triplet states will be discussed. The changes in  $\pi$ -electron structure of the systems under investigation will be assessed by means of the Substituent Effect Stabilization Energy (SESE) parameter [4] and by the set of commonly used aromaticity indices.

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[2] Dobrowolski, M.A., Kaniewski, J., Krygowski, T.M., Cyrański, M.K., *Collect. Czech. Chem. Commun.*, 74:115-129, 2009.

[3] Krygowski, T.M., Dobrowolski, M.A., Cyrański, M.K., Ozimiński, W.P., Bultinck, P., *Comput. Theo. Chem.*, 984:36-42, 2012.

[4] Pross, A., Random, L., Taft, R.W., *J. Org. Chem.*, 45:818-826, 1980.