

## A DFT COMPARATIVE STUDY OF SUBSTITUENT EFFECTS IN RADICALS, CATIONS AND RADICAL CATIONS

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In contrast to organic radical centers where both electron donating and withdrawing groups are usually stabilizing, substituent effects are varied in charged intermediates such as cations and anions. Hence it is interesting to consider the effect that substituents exert in open shell systems which are also charged, i.e. radical cations and radical anions.

We describe a DFT computational study where substituent effects in such intermediates as they occur in ethylene and benzene and derivatives are quantified in terms of stabilisation energies obtained through the application of isodesmic equations. Charge and spin distributions in the various species are also examined.

It has previously been shown that cyclisation reactions of alkenyl and aryl alkanols can occur via complementary mechanisms involving either alkoxy radical or alkenyl and aryl radical cation intermediates.<sup>[1]</sup> The implications of the current theoretical study for reactivity and regioselectivity in such systems are discussed.

The calculations have employed the global hybrid generalized gradient approximation (GH-GGA) functional, B3LYP, as well as two of the more recent range separated generalised gradient approximation (RSH-GGA) hybrid functionals,  $\omega$ B97X-D and  $\omega$ B97X-V, both of which incorporate additional features to account for dispersive interactions.<sup>[2]</sup> The large 6-311+G(2DF,2P) basis set that contains diffuse and polarization functions for all the elements involved was employed in all calculations.

### REFERENCES

- [1] C.W. McClelland, G.D. Ruggiero, I.H. Williams, *J. Chem. Soc. Perkin Trans.* **2002**, 2, 204–208 and references cited therein.
- [2] N. Mardirossian, M. Head-Gordon, *Molecular Physics*, **2017**, *115*, 2315–2372; N. Mardirossian, M. Head-Gordon, *J. Chem. Phys.*, **2018**, *148*, 241736 and references cited therein.