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# On the ring-opening of substituted cyclobutenes to benzocyclobutenes

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## Résumé

Recently it has been proven that trans-disiloxybenzocyclobutene combines easily with dioxygen in its triplet state.(a) This opens the perspective of new, stable molecules capable of catching radical systems. The rate limiting step of this reaction is the ring-opening of the substituted benzocyclobutene, which, moreover, is endothermic.

We present in this contribution a careful computational analysis and quantification of effects that play a role in the reaction energy of the ring-opening in substituted cyclobutene. Those effects include hyperconjugation,  $\pi$  delocalization, ring strain and aromaticity. It is found that the energy difference between closed and open forms are dictated mainly by the electronic structure of the open form, in which the rotation along the resulting simple C-C bond drives the electronic delocalization. Our calculations lead us to quantify effects that determine the energy difference in the special case of disubstituted benzocyclobutene with respect to the disubstituted o-xylylene. The role of the siloxo-substituents is clarified by an analysis of the molecular orbitals. From a computational point of view, the agreement on reaction energies from several Density Functional Theory methods have been tested against high-level reference calculations (CCSD(T)).(b)

(a) J. Drujon, R. Rahmani, V. Héran R. Blanc, Y. Carissan, B. Tuccio, L. Commeiras and J.-L. Parrain, PCCP, **2014**, 7513-7520.

(b) P. Nava and Y. Carissan., submitted.

**Mots-Clés:** aromaticity,  $\pi$  delocalization, substituent effect, DFT

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