GROUND AND EXCITED STATES OF *M*-PHENYLENECARBENONITRENES

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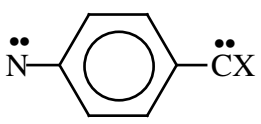
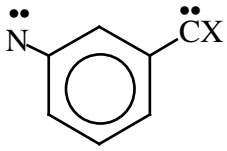
p-Phenylenecarbenonitrenes **1-X**, **X** = H, F, Cl, Br have been observed and studied computationally.[1] Calculations indicated that the halogen substituent can influence significantly the "local" electronic configuration at the carbene center affecting, thus, the relative energies of electronic states of different multiplicities. Despite this all species were predicted to have singlet ground states in agreement with the experimental results.

Herein, recent work on the meta isomers **2-X**, **X** = H, F, Cl, Br will be presented. Geometries (B3LYP, MCSCF) and relative energies (CASPT2, QCISD(T)) of various electronic states have been computed. According to these calculations the effect of the substituent is more dramatic in **2-X** than in **1-X**, resulting in a change of the ground-state multiplicity. Thus, while **2-H** is known to have a quintet ground-state,[2] **2-F** is found to have a triplet one.



1-X



2-X

1) Nicolaides, A.; Enyo, T.; Miura, D.; Tomioka, H. *J. Am. Chem. Soc.* **2001**, *123*, 2628.

2) Tukada, H.; Mutai, K.; Iwamura, H. *J. Chem. Soc., Chem. Comm.* **1987**, 1159.