COMPUTATIONAL STUDY OF C–H⋯π INTERACTIONS OF ACETYLENE AND DIACETYLENE WITH METHYL- AND FLUORO-SUBSTITUTED BENZENE

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Abstract: Benzene-acetylene complex is a prototype system for C-H⋯π interactions. Understanding of noncovalent interactions of C-H⋯π type has been given importance due to their presence in biological systems, crystal structures, materials science and organic chemistry. We have investigated the effect of tri- and hexa- substitutions of –CH₃ and –F groups to benzene on C-H⋯π interactions using recently developed M06-2X density functional. We have considered acetylene and diacetylene as source of Hydrogen for C-H⋯π interactions. All the geometry optimizations and harmonic vibrational frequency calculations were performed using M06-2X/6-31+G(d,p) level in Gaussian '09 program. We measured the binding energy, the distance between H of C-H and the center of π-system. The characteristic C-H stretching vibrational frequencies and frequency shifts were analyzed. Basis Set Superposition Error (BSSE) was corrected by applying Counter Poise (CP) technique proposed by Boys and Bernardi. We also determined the Mulliken charges of the Hydrogens of acetylene and diacetylene to better describe the change in binding energy. We also performed the energy decomposition analysis (EDA). It was calculated by ADF 2013 using M062X/Aug-ATZ2P. The binding energy term was split into Electrostatic Energy, Pauli's repulsion energy, Orbital Interaction energy etc. We compared our results with available experimental data. For example, binding energy for benzene-acetylene complex was experimentally found. The calculated binding energy for the above complex is 2.82 kcal/mol, which is in excellent agreement with the experimental result of 2.7 ± 0.2 kcal/mol. Our study shows that the C-H⋯π binding strength increases by increasing the substitution of electron donating group (-CH₃) with benzene. In contrast, the binding strength decreases by increasing the electron withdrawing group (-F). Importantly, the binding energy strength increases when we move from acetylene to diacetylene. The binding strength correlates with the distance between H of C-H and the center of π-system. We have noticed red-shift or blue-shift for C-H stretching frequency of C-H⋯π interactions for the considered complexes.