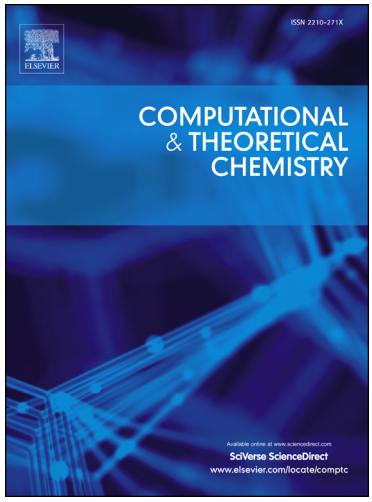

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The Equilibrium Geometries of Heptatriynylidene, Cyclohepta-1,2,3,4-tetraen-6-yne, and Heptahexaenylidene

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Abstract

The equilibrium geometries of heptatriynylidene (**1**), cyclohepta-1,2,3,4-tetraen-6-yne (**2**), and heptahexaenylidene (**3**) have been theoretically investigated at various level of theories. The methods employed are Møller-Plesset perturbation level of theory until second-order, coupled-cluster singles and doubles (CCSD), and CCSD via perturbative triple excitations [CCSD(T)]. Correlation consistent polarized valence double and triple zeta (cc-pVXZ; X = D and T) basis sets are used in all calculations, which are compatible with the frozen-core approximation entreated in this study. The relative energies of the ground triplet electronic state ($\widetilde{X}^3\Sigma_g^-$) of **1** - the most stable isomer of C_7H_2 - to the ground singlet electronic states of **2** ($\widetilde{X}^1A_1$) and **3** ($\widetilde{X}^1A_1$) have also been estimated at different levels. With zero-point vibrational energy corrections, **2** and **3** are found to lie $\sim$ 12.27 and $\sim$ 20.62 kcal mol^{-1}, respectively, above **1** at the highest level of theory (CCSD(T)/cc-pVTZ). While **1** and **3** are observed in the laboratory, **2** is a hypothetical molecule hitherto. Since the optimal geometry of **2** suggests the presence of biradical character, the singlet-triplet ($\widetilde{X}^1A_1$-$^3B_1$) energy gap for isomer **2** was also calculated at various levels. The *a*b initio data presented here may be useful for the laboratory detection of **2** and astronomical detection of **2** and **3**.

Keywords: Heptatriynylidene, Cyclohepta-1,2,3,4-tetraen-6-yne, Heptahexaenylidene, Cumulene carbene, Equilibrium geometry, Astronomical detection

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