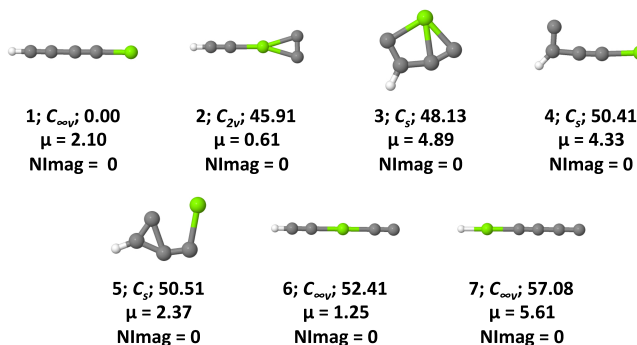


## COMPUTATIONAL STUDIES OF $\text{MgC}_4\text{H}$ ISOMERS

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Constitutional isomers of  $\text{MgC}_4\text{H}$  elemental composition are theoretically investigated in this work using density functional theory at various levels. The linear doublet ( $^2\Sigma^+$ ) isomer, 1-magnesapent-2,4-diyne-1-yl (**1**), was identified not only in the laboratory but also in the evolved carbon star, IRC+10216. While zero-point vibrational energy corrected relative energies obtained at the ROB3LYP/6-311++G(2d,2p) and  $\text{RO}\omega\text{B97XD}/6\text{-}311\text{++G}(2\text{d},2\text{p})$  levels correctly predict that isomer **1** is the global minimum geometry, the same obtained with UHF wavefunctions predict that a cyclic isomer, 1-ethynyl-1- $\lambda^3$ -magnesacycloprop-2-yne (**2**), is the global minimum structure. Further electronic structure calculations carried out with GGA-functional, such as PBE0-D3 with def-TZVP basis set predict that isomer **1** is the global minimum irrespective of whether the solutions are based on ROHF or UHF wavefunctions. It is outlined here that the issue of spin-contamination (though under 5 %) becomes a serious one affecting the relative energies dramatically while using hybrid functionals such as B3LYP and  $\omega\text{B97XD}$  in this case.



**Figure 1:** Isomers of  $\text{MgC}_4\text{H}$ . Relative energies (in  $\text{kcal mol}^{-1}$ ) and dipole moments (in Debye) are computed at the UPBE0-D3/Def2-TZVP level. All isomers are minima.