

Abstract

The work presents, for the first time, the matrix isolation infrared and *ab initio* studies on the molecular conformations of 2-butyne-1, 4-diol. It is found that when the acetylenic moiety ($-\text{C}\equiv\text{C}-\text{H}$) in propargyl alcohol is replaced by a CH_2OH group, it gives rise to many different conformations of ethylene glycol, which are facilitated by strong intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonded interactions. Similarly, when the acidic hydrogen in propargyl alcohol is replaced by a CH_2OH group, several conformations arise for 2-butyne-1, 4-diol. Thus, these molecules, propargyl alcohol, ethylene glycol and 2-butyne-1,4-diol provide an interesting case to study the effect of an acetylenic π cloud between the two $-\text{OH}$ groups on the conformations, which was absent in ethylene glycol. Starting from only two stable conformers in propargyl alcohol and ten stable conformers in ethylene glycol, we have computed six stable conformers of 2-butyne-1,4-diol in this work at M06-2X and MP2 methods employing 6-311++G** and aug-cc-pVDZ basis sets. Our experiments together with computations revealed the presence of three most stable conformers in the N_2 matrix. AIM and NBO analysis have been performed to understand the nature of interactions in the conformers. Vicinal orbital interactions are found to play a deciding role in its conformational preference.

Competitive hydrogen bonding because of the presence of multiple bonding sites in 2-butyne-1, 4-diol is another aspect which we have explored from our computational studies on its hydrogen-bonded complexes with water.