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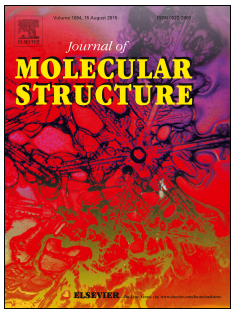

A computational study of the interplay of steric and electronic effects in the stabilization of 1,3-(diamino)oxyallyls

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A computational study of the interplay of steric and electronic effects in the stabilization of 1,3-(diamino)oxyallyls

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Abstract: Ring opening of cyclopropanones affords non-Kekulé oxyallyls, which are usually fleeting intermediates. However, recent experimental results showed that amino-substituted versions can be stable enough to be characterized in solution by NMR spectroscopy. Herein, the role of substituents in the stabilization of oxyallyls was examined by DFT calculations at the B3LYP/6-311g(d,p) level of theory. The stability of model compounds, relative to their cyclic structural isomers, was evaluated for simple substituents covering a broad range of electronic properties. The particular case of the model 1,3-bis(amino)oxyallyl (H2N)CHCOCH(NH2) has been examined from a conformational standpoint to shed light on the interplay of sterics and electronic influence of the amino substituents. Finally, model tetrasubstituted di(amino)oxyallys were considered and provided few general guidelines for the design of new stable derivatives with oxyallyl patterns.

Graphical Abstract