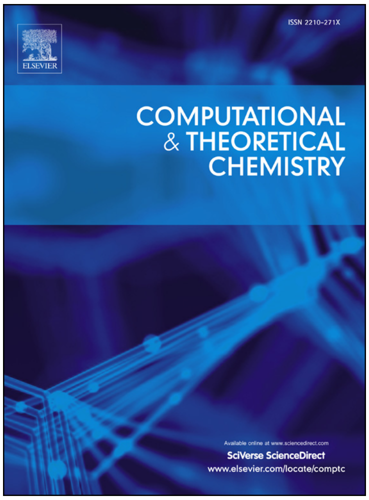

Isomerization Barriers for the Conrotatory and Disrotatory Isomerizations of 3-aza-Dihydrobenzvalene to 1,2-Dihydropyridine and 3,4-diaza-Dihydrobenzvalene to 1,2-Dihydropyridazine

Jeffrey D. Veals, Steven R. Davis

PII: S2210-271X(13)00306-X
DOI: http://dx.doi.org/10.1016/j.comptc.2013.07.019
Reference: COMPTC 1188

To appear in: *Computational & Theoretical Chemistry*

Please cite this article as: J.D. Veals, S.R. Davis, Isomerization Barriers for the Conrotatory and Disrotatory Isomerizations of 3-aza-Dihydrobenzvalene to 1,2-Dihydropyridine and 3,4-diaza-Dihydrobenzvalene to 1,2-Dihydropyridazine, *Computational & Theoretical Chemistry* (2013), doi: http://dx.doi.org/10.1016/j.comptc.2013.07.019

Isomerization Barriers for the Conrotatory and Disrotatory Isomerizations of 3-aza-Dihydrobenzvalene to 1,2-Dihydropyridine and 3,4-diaza-Dihydrobenzvalene to 1,2-Dihydropyridazine

Jeffrey D. Veals[‡] and Steven R. Davis[*]

Department of Chemistry and Biochemistry, University of Mississippi, University, MS 38677

[‡] *Current Address: Department of Chemistry, University of Missouri, Columbia, MO 65211*

Abstract

The isomerizations of 3-aza-dihydrobenzvalene to 1,2-dihydropyridine and 3,4-diaza-dihydrobenzvalene to 1,2-dihydropyridazine have been studied using ab initio methods with a multiconfigurational wavefunction. Transition states for both the allowed, conrotatory and forbidden, disrotatory reaction channels were located. The isomerizations occur through the cleavage of a bond pair in the bicyclobutane moiety. The four allowed pathways for 3-aza-dihydrobenzvalene isomerization are nonconcerted forming intermediates with a trans double bond in a six-membered ring: two isomers of (E,Z)-2,4-dihydro-1,6-pyridine and two isomers of (Z,E)-2,4-dihydro-1,6-pyridine. These intermediates can isomerize to the final 1,2-dihydropyridine product through trans double bond rotation with barriers of only a few $\mathrm{kcal \cdot mol^{-1}}$. The allowed pathways have initial activation barriers which range from 35.6 to 42.2 $\mathrm{kcal \cdot mol^{-1}}$. The four forbidden pathways lead directly to the final 1,2-dihydropyridine product in a concerted mechanism with transition states of substantial singlet biradical character. Their activation barriers range from 47.0 to 56.1 $\mathrm{kcal \cdot mol^{-1}}$. The two allowed pathways for 3,4-diaza-dihydrobenzvalene isomerization are also nonconcerted forming two isomers of (E,Z)-3,5-dihydro-1,2-pyridazine intermediates which then isomerize to 1,2-dihydropyridazine through trans double bond rotation with barriers of only about 2 $\mathrm{kcal \cdot mol^{-1}}$. The initial barriers for the two allowed pathways are 32.0 and 41.6 $\mathrm{kcal \cdot mol^{-1}}$ with one pathway substantially