Reluctance towards Aromatization of Vinamidine Analogues into Substituted Pyridines.
A Theoretical Evaluation of the Reaction Mechanisms that Never were

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Computational Chemistry not only offers insight into the electron causality of chemical reactions, but may also shed some light on unexpected chemical behavior by scrutinizing possible outcomes for an unobserved process. Despite our many experimental efforts, the title compounds failed to aromatize to the corresponding pyridines, even when the latter should be more stable. Orbital, electronic and energetic arguments are presented herein, in order to rationalize this reluctance. QST2, QST3 and IRC calculations through Density Functional Theory (with various functionals) were carried out to evaluate two plausible intramolecular reaction mechanisms, named Path A and Path B (Figure 1, top). Thus, reversed *reductio ad absurdum* reasoning leads us to the observation that activation barriers are too high for the transformation to occur despite the gain in stability.

A push-pull system is observed to influence the increased stability of the non-aromatic compounds as observed at the bottom of Figure 1, where bonding orbitals (left) create an in phase electron corridor and anti-bonding orbitals (right) form an out of phase electron corridor.

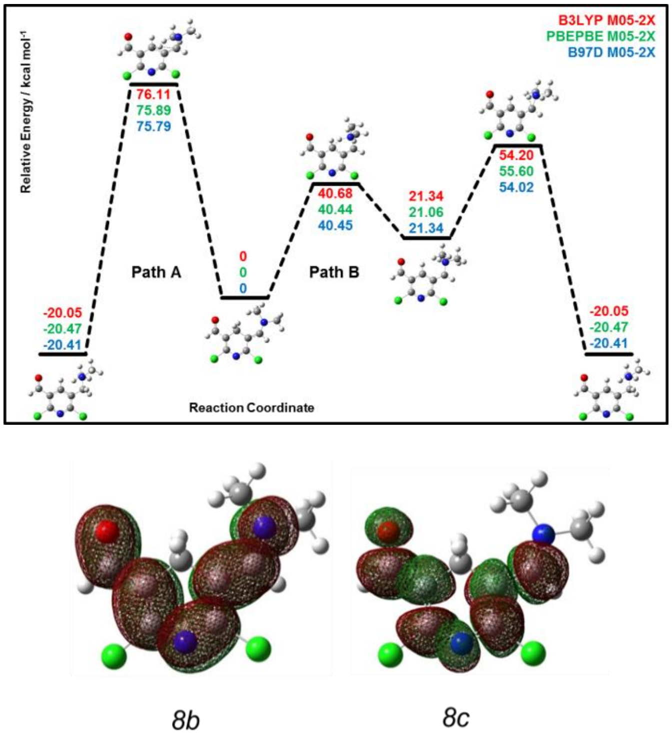

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Figure 1