DFT STUDIES OF THE β-AMINOPROPIOAMIDOXIMES ARYLSULFOCHLORINATION PRODUCTS

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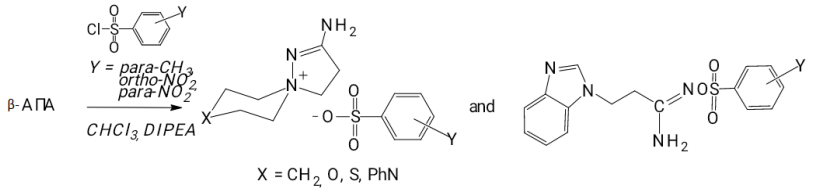
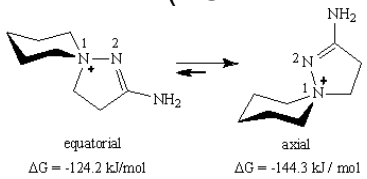
Earlier we reported an unusual course of the reaction of tosylation and *ortho*-, *para*-nitrophenylsulfochlorination of β-aminopropioamidoximes (β-APA) in the presence of diisopropylethylamine (DIPEA). As it was shown by experiment and by DFT theoreticalcalculations performed at the B3LYP/6-31++G(d,p) level for β-APAs with β-aminogroups (piperidin-1-yl, morpholin-1-yl, thiomorpholin-1-yl, 4'-Ph-piperazin-1-yl) the formation of the new spiropyrazoline systems is thermodynamically favourable: ΔG varies from -119.9 to -163.6 kJ/mol. But the spiropyrazoline structure for β-(benzimidazol-1-yl)propioamidoxime has not been experimentally formed as it is thermodynamically unfavorable (ΔG = 45.9and 20.0 kJ/mol for tosylation tosylation and *para*-nitrophenylsulfochlorination of β-APAs); only products at O-atom of the amidoxime group were isolated [1].



It was demonstrated on the example of piperidine spiropyrazolinium tosylate that the axial position of the nitrogen (N2) of the pyrazolinium heterocycle in respect to the six-membered cycle is more preferable (ΔG = -144.3 kJ/mol) than the equatorial one (ΔG = -124.2 kJ/mol).



However, recently for a series of solid 2-amino-1,5-diazospiro[4.5]dec-1-en-5-ammonium nitrobenzene sulfonates the axial conformer was detected by means of XRD techniques [2]. For all studied compounds, the energies of the frontier orbitals were calculated; negative LUMO values determine them as nucleophiles.

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References

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