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STUDIES ON NITROGEN LONE-PAIR ORIENTATION AND NONBONDED n-π INTERACTION IN N-HETEROCYCLIC COMPOUNDS

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Summary

Spectroscopic studies of homoallyl and bishomoallyl types of nonbonded n-π interaction in heterocyclic compounds are reported. Nitrogen lone-pair orientations in N-methyl-7-azabenzonorbornadiene, N-methyl-7-azanorbornadiene-2,3-dicarboxylic acid and 2-aza-5-norbornene were determined by the use of shift reagent induced paramagnetic nmr shifts. Nitrogen lone-pair is generally oriented more favourably at the anti position with respect to the nonadjacent double bond. In order to study the nonbonded n-π electronic interaction, the photoelectron, UV and fluorescence spectra were also obtained for these azabicyclic imines and other five and six-membered cyclic imines. It was found that perturbation of nitrogen lone-pair ionization potential induced by the interaction with nonadjacent carbon-carbon double bond and UV and fluorescence spectra due to $n-\pi^*$ interaction are quite different between β,γ-unsaturated five-membered cyclic imines and β,γ-unsaturated six-membered imines. These observations were discussed in terms of different manner of n-π homoallyl and bishomoallyl interactions based on the difference in molecular symmetry, lone pair ionization potential and stereospecific orientation of nitrogen lone pair electrons in cyclic and bicyclic imines.