
Abstract

The structural stability and internal rotation of the formyl group in 1-formylazirine and 3-formyldiazirine were investigated by ab initio MP2 and DFT-B3LYP calcns. with 6-311+G** basis set. From the calcns. 1-formylazirine was found to exist predominantly in gauche (carbonyl C=O group nearly eclipses ring C-N bond) conformation, while 3-formylazirine to exist in cis .tautm. trans conformational equil. For 3-formyldiazirine the cis (C=O moiety eclipses the ring) and the trans (C=O moiety eclipses the α-hydrogen of the ring) conformers were predicted to have a comparable relative stability with cis to trans rotational barrier of about 9 kcal/mol. The equil. const. for the cis .tautm. trans interconversion in 3-formyldiazirine was estd. to be 0.2914 that corresponds to an equil. mixt. of about 23% cis and 77% trans at 298.15 K. The vibrational frequencies were computed at DFT-B3LYP level for the gauche 1-formylazirine and the cis and trans mixt. of 3-formyldiazirine. Normal coordinate calcns. were carried out and the potential energy distributions PED were calcld. for the stable conformers of each of the two mols.