

Normal coordinate analyses and barrier to internal rotation of nitroso- and nitroazides.

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Abstract

The conformational and structural stability of nitrosoazide NNN-N:O and nitroazide NNN-NO₂ were investigated by DFT-B3LYP and ab initio MP2 calcns. with 6-311++G** basis set. From the calcns., nitrosoazide was predicted to exist predominantly in the planar trans (NNN and N:O groups are trans to each other) structure with high trans-cis rotational barrier of about 11 kcal mol⁻¹ as a result of pronounced conjugation between the azide group and the N:O bond. The NO₂ rotational barrier in nitroazide was predicted from the sym. potential function to be of about 7 kcal mol⁻¹. The vibrational frequencies were calcd. at the DFT-B3LYP level and the IR and Raman spectra of the cis-trans mixt. were plotted. Complete vibrational assignments were made on the basis of normal coordinate calcns. for the stable conformers of both mols. For nitrosoazide, the calcd. wavenumbers were compared to the corresponding exptl. values obtained from early reported Raman spectrum of the mol.