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N-TRIFLUOROACETYLPIPERIDINE – A FIRST EXPERIMENTALLY STUDIED GAS-PHASE ‘NON-CONFORMERIC’ STRUCTURE WITH 9-ATOMS PLANAR CONFIGURATION AT NITROGEN ATOM

The conformational preference of a N-alkyl piperidines is equatorial due to 1,3-diaxial repulsion effects which destabilize the axial conformer. However, in N-alkenyl, alkynyl or phenyl-piperidines, the hyperconjugation between the electron lone pair on nitrogen atom and the π -system of substituents raises stability of the axial form [1,2]. As follows from the quantum chemical (QC) calculations, all N-substituted piperidines may be divided by three groups depending on the equatorial : axial forms ratio [1].

In this study, the molecular structure of N-trifluoroacetylpiperidine **1** was studied by gas electron diffraction (GED), IR spectroscopy and QC calculations. Geometry optimization and vibrational calculations were performed at the DFT (with B3LYP, B3LYP-GD3 and M06-2X functionals) and MP2 levels with 6-311G** and cc-pVTZ basic sets.

Four transition states and one minimum were located in the potential energy surface (PES) profile, obtained by rotating the substituent around the N–C α bond, see Fig. 1. Electron energies of these states are by *ca.* 20 kcal/mol above than optimal structure.

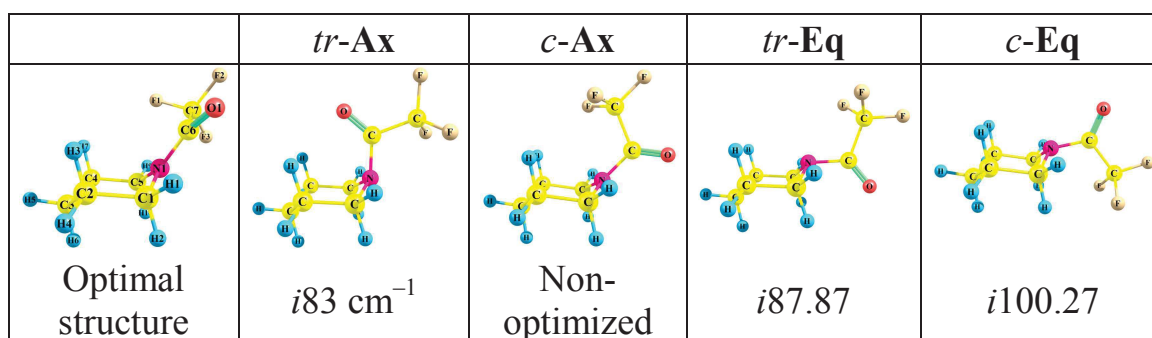


Fig. 1. Molecular structure of **1** and its transition states

It was found that in the optimal structure the nitrogen bond configuration is nearly planar, with $\sum \angle \text{CNC} = 357\text{--}360^\circ$ (QC) and $360 \pm 3^\circ$ (GED), i.e. the compound **1** may exist in a form of the only conformer, in which the trifluoroacetyl group substitutes occupies intermediate, between equatorial and axial positions. Nine atoms (two equatorial H atoms in C α -

positions, two C_α atoms, the nitrogen atom, the carbonyl group and one CF fragment of trifluoromethyl group) lie in one plane. The φ angle between the plane containing the carbonyl group and the plane of piperidine ring frame is 51–52° (B3LYP), 60–61° (B3LYP-GD3), 62–64° (M062X), 63–69° (MP2) and 53(2)° (GED). Substitution of the hydrogen atoms in the acetyl group by fluorine atoms in N-acetylpiperidine slightly decreases the φ angle due to increase of steric repulsion.

Comparison of experimental and theoretical IR spectra shows that the DFT method with B3LYP and B3LYP-GD3 functionals very well predicts bands in the regions 1100–1320 and 1400–1520 cm⁻¹. From the other calculations, these bands slightly shifted to violet region as compared with the experimental one. According to the QC calculations, the vibrational wavenumber of carbonyl group is 1753–1769 (B3LYP and B3LYP-GD3), 1777 cm⁻¹ (MP2). These values are by *ca.* 67 cm⁻¹ (B3LYP and B3LYP-GD3) and *ca.* 84 cm⁻¹ (MP2) shifted to violet region compared to the experimental bands. At the same time, the M062X calculations predict this band to be 1814–1830 cm⁻¹, which is by 127 cm⁻¹ away from the experimental data.

The orbital interaction energy between the Lp on the nitrogen atom and the carbonyl group Lp(N)→BD*(C6,O) of **1**, is very high, 70–74 (B3LYP) to 96–110 (MP2) kcal/mol, that leads to planar nitrogen bond configuration. Because of this, the MP2 method predicts that φ angle to be larger than one from B3LYP calculations. Due to high orbital interaction energy, the nitrogen bond configuration is nearly planar, making impossible to assign this molecule to neither axial, nor equatorial conformation, but to ‘intermediate’ one.

REFERENCES

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2. Shlykov S.A., Phien T.D., Gao Y., Weber P.M., *J. Mol. Struct.* **2017**, *1132*, 3-10.