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THEORETICAL EVALUATION OF THE GEOMETRY AND CONFORMATIONAL PROPERTIES OF OXONIUM AND AMMONIUM IONS OF TETRA-HYDRO-1,3-OXAZINE

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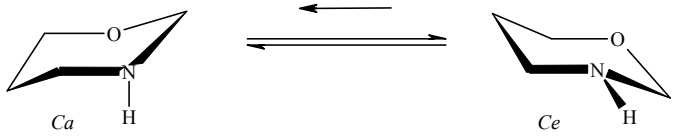
Tetrahydro-1,3-oxazines are asymmetrical 1,3-heteroanalogs of cyclohexane. These compounds display structural features, which are largely a function of the conformational behavior of the nitrogen atom. Interest in these compounds is related to these structural features as well as to their valuable pharmacological properties and use as reagents for fine organic synthesis [1, 2]. A calculation of the conformational equilibrium of tetrahydro-1,3-oxazines using semiempirical approximations supported the experimental data indicating predominance of the *Ca* conformation in the mixture [3].



In the present work, we carried out an *ab initio* RHF/6-31G(d) calculation using the Hyperchem program package [4] for the first time relative to the stability of the ammonium and oxonium ions of tetrahydro-1,3-oxazine formed as a result of protonation in the initial stage of opening of the heterocycle ring [5].

This calculation indicated that the ions studied are exothermic ($\Delta H < 0$). The axial form *Ca* of the initial tetrahydro-1,3-oxazine, relative to which the value of ΔH was calculated, was shown to be 3.2 kcal/mol more stable than the *Ce* conformer according the RHF/6-31G(d) calculation. All the ions show bond lengths and bond angles in the heteroatomic fragment of the ring different from those in the starting oxazine. The molecule of the more labile oxonium ion is markedly distorted due to a significant extension of the C(2)–O bond and a much shorter C(2)–N bond.

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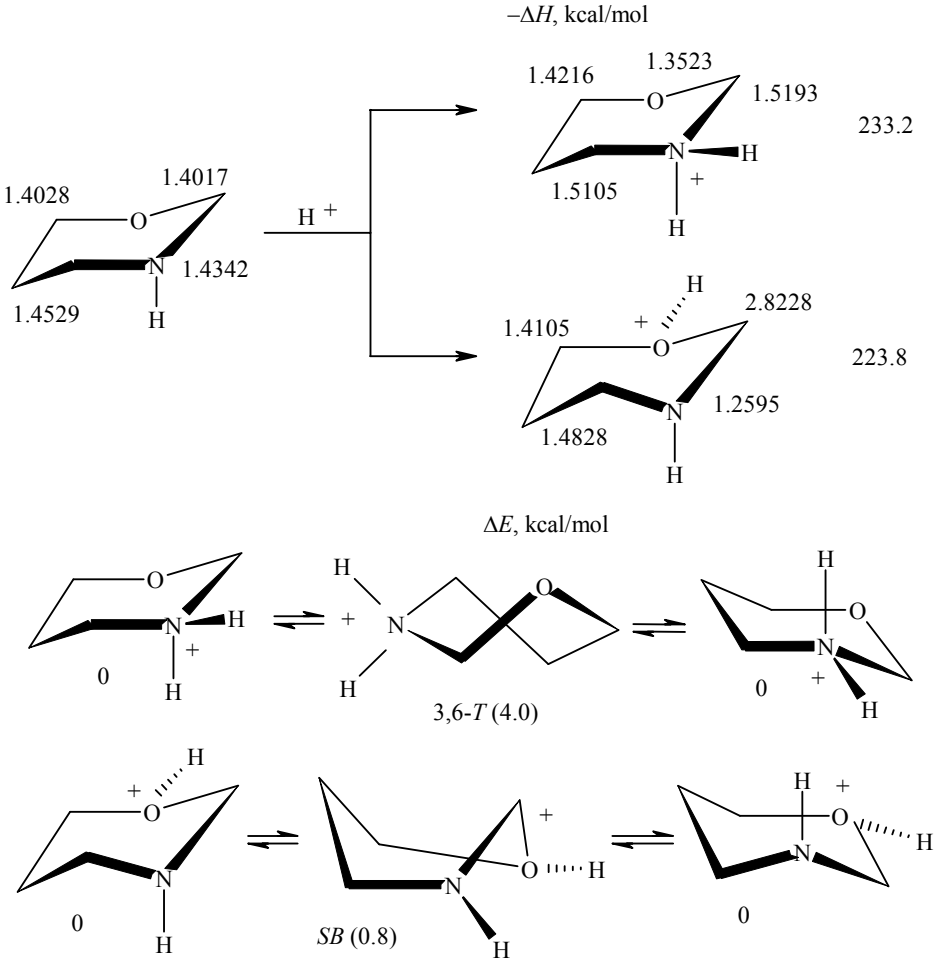
The computer modeling indicated the possibility of conformational transformations of the ammonium and oxonium ions to give alternative forms degenerate in energy through intermediate minima: the 3,6-*twist* (3,6-*T*) and distorted *symmetrical boat* conformers (*SB*).

Lengths of the C-O and C-N Bonds, Å



These results show that protonation, which should occur predominantly at the nitrogen atom, markedly alters the geometry of the 1,3-oxazine ring and affects its conformational properties. The approach employed opens additional possibilities for studying the mechanisms of the chemical transformations of these compounds.

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