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LETTERS TO THE EDITOR

Conformational Conversions in Perhydro-1,3,5-dithiazine

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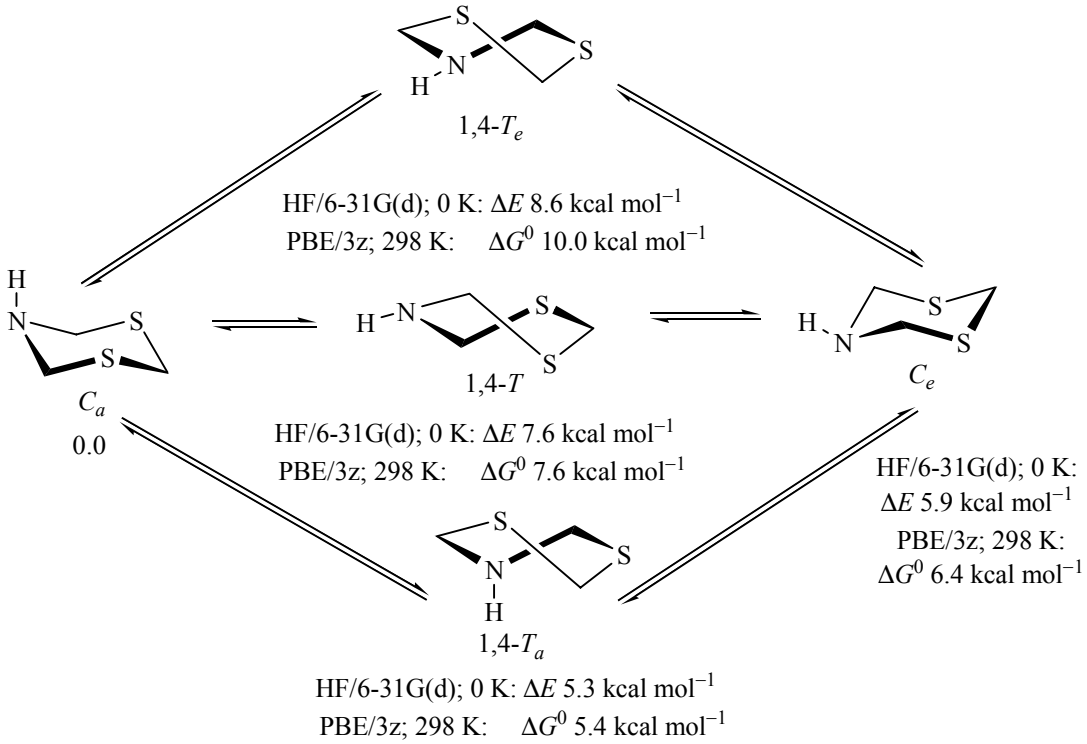
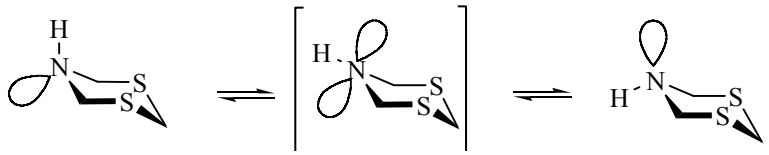
The interest in structural investigations of perhydro-1,3,5-dithiazines, the saturated hetero analogs of cyclohexane with three heteroatoms located in the meta-positions of the ring, is associated with their structural features, presence of valuable pharmacological and sorption properties, as well as with their use as reagents in fine organic synthesis [1–5]. X-ray diffraction data indicate the predominant *chair* conformation, which is characteristic of these molecules [6]. However, the conformational conversion of compounds of this class so far remained unexplored. In this paper the conformational isomerization of perhydro-1,3,5-dithiazine was studied for the first time by means of non-empirical approximation HF/6-31G(d) (HyperChem software [7]) and DFT method PBE/3z (PRIRODA package [8]) we for the first time studied the conformational isomerization of perhydro-1,3,5-dithiazine.

We found that the potential energy surface (PES) of the studied compound contains several minima corresponding to the equatorial and axial chair





C_a TS C_e

HF/6-31G(d); 0 K: $\Delta E^{\neq}$ 8.0 kcal mol^{-1}
PBE/3z; 298 K: $\Delta G^{\neq}$ 6.7 kcal mol^{-1}

conformers (C_e, C_a), and flexible 1,4-*twist* and 2,5-*twist* forms (1,4-T_e , 1,4-T_a, 2,5-T). The main minimum corresponds to the form C_a, and the intermediate minima correspond to conformers of C_e, 1,4-T_e, 1,4-T_a, and 2,5-T. Within the used approximations, a minimum on the PES closest to the C_a conformer is the form 1,4-T_a.

The conformational isomerization $C_a \leftrightarrow C_e$ may be also due to the pyramidal inversion of nitrogen; this route includes a transition state (TS) corresponding to its planar configuration.

It should be noted that the calculated potential barrier of the considered process [HF/6-31G(d)] is close to the experimental value for trimethylamine and six-membered heterocyclic compounds with one nitrogen heteroatom (8.2–8.3 kcal mol^{-1} [9]).

The results show that in the conformational equilibrium of unsubstituted perhydro-1,3,5-dithiazine the C_a form largely dominates, while the contribution of conformers 1,4-T_a and C_e is relatively low.

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