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LETTERS TO THE EDITOR

CONFORMATIONAL ISOMERISM OF 3-ISOPROPYL-1,3-DIOXANE

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The interest in the structure of 1,3-dioxanes is related both to unique features of these compounds and their use as reagents in fine organic synthesis [1-3]. The potential energy surfaces of unsubstituted dioxane and 2-methyl-1,3-dioxanes contain *chair* (*C*) (or equatorial (*Ce*) and axial chair conformers (*Ca*) for monosubstituted dioxanes) as well as flexible 1,4-*twist* (1,4-*T*) and 2,5-*twist* (2,5-*T*) forms as local minima. In the present work, we have carried out the first study of the conformational isomerization of 5-isopropyl-1,3-dioxane using the HyperChem program package [9] with nonempirical RHF//STO-3G and 6-31G(d) quantum-chemical approximations.

The ^{1}H NMR spectral data indicate that the conformational equilibrium of these molecules at room temperature is shifted toward the *Ce* form [2].

ΔG^0 = 0.98-1.10 kcal/mol

The present results indicate two pathways for the *Ce* → *Ca* conformational isomerization analogous to those observed for unsubstituted dioxane and 2-methyl-1,3-dioxanes [4-6]. In this case, conformational equilibrium is possible both between the *chair* and *twist* forms and between the two flexible forms. The major minimum corresponds to the *Ce* conformer. Thus, the potential energy surface of the compound studied contains the same minima as for 2-methyl-1,3-dioxane [6]. However, the difference in energy between the *Ce* and *Ca* forms in the case of the 5-isopropyl analog is significantly less. This difference using the 6-31G(d) basis corresponds to the experimental ΔG^0 value [2]. The most labile minimum in all cases corresponds to the 1,4-*T* conformer.

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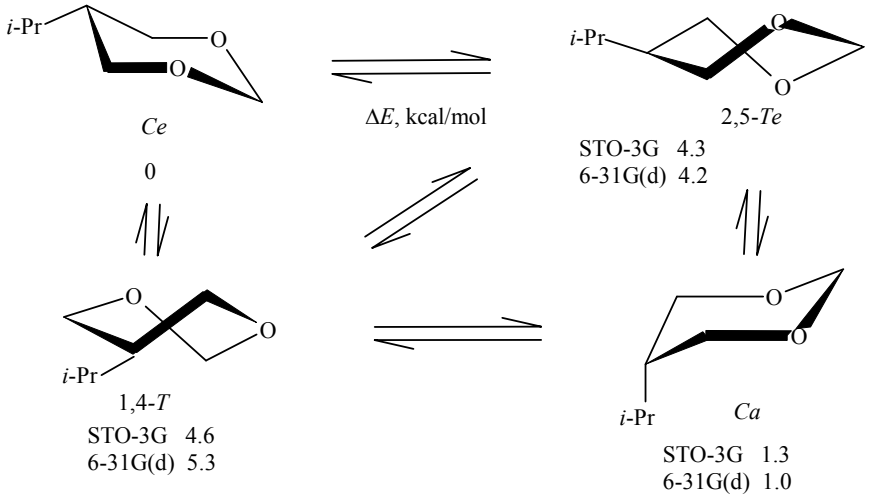
These findings indicate greater conformational flexibility for 5-isopropyl-1,3-dioxane molecules in comparison with the 2-methyl analog [6] due to the less significant steric interaction of the axial alkyl group at atom C-5 with the hydrocarbon fragment of the ring.



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