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CONFORMATIONAL ISOMERIZATION OF 4-METHYL-1,3-DIOXANE

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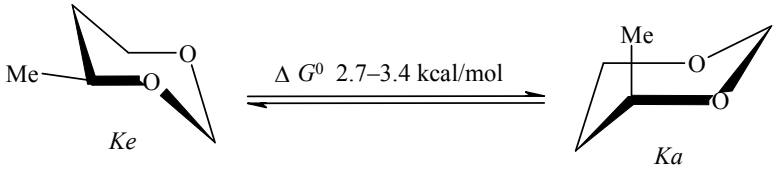
The whole possible course of conformational isomerization of 4-methyl-1,3-dioxane has been established using empirical (MM+) and nonempirical [STO-3G, 3-21G, 6-31G(d) and 6-31G(d,p)] approximations within the limits of the Hartree-Fock method. It was shown that the potential energy surface of this compound contains a principal (equatorial chair conformer) and local minima corresponding to the axial chair conformer and series flexible forms.

Keywords: 4-methyl-1,3-dioxane, quantum chemistry, conformer, conformational equilibrium, *chair* form, potential energy surface.

The interest in 1,3-dioxane, connected with its characteristic structure, chemical behavior, and a complex of practically applicable properties [1], provides an urgency for the study of the potential energy surface of the molecule of these compounds by computer modeling [2-7]. The present work is associated with an investigation of the means of conformational isomerization of 4-methyl-1,3-dioxane using an empirical method (MM^+) and also nonempirical methods (STO-3G, 3-21G, 6-31-G(d), and 6-31G(dp)) within the limits of the Hartree-Fock quantum-chemical approximation under conditions for modeling the behavior of the molecule in the gas phase within the limits of the HyperChem program [8].

It is known that the principal minimum on the potential energy surface of 1,3-dioxanes corresponds to the *chair* conformer with the equatorial orientation of the axial substituent (*Ke*). ^{1}H NMR Spectroscopic data show unambiguously the existence of the 4-methyl-1,3-dioxane molecule at room temperature predominantly in the *Ke* form with sufficiently large free conformational energy of the methyl group [9].



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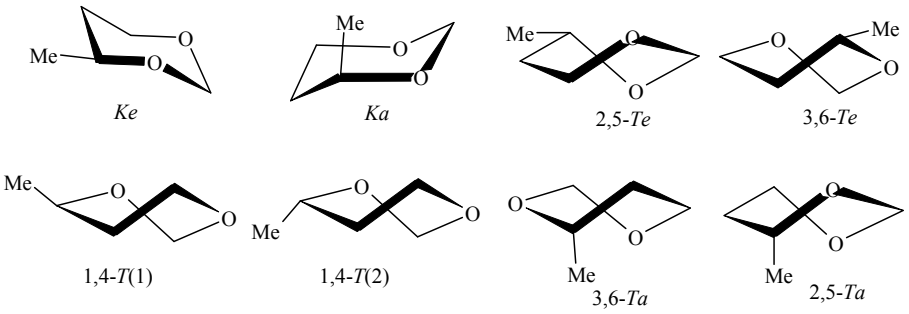
We have identified for the first time the general diagram for the conformational conversion and also the character of the intermediate minima on the potential energy surface of this compound. It proposes several routes for the conformational isomerization *Ke*↔*Ka*, differing to a large extent in the participation in flexible forms: 1,4-, 2,5-, and 3,6-*twist* (1,4-, 2,5-, 3,6-*T*) with axial (*a*) and equatorial (*e*) orientation of the methyl substituent.



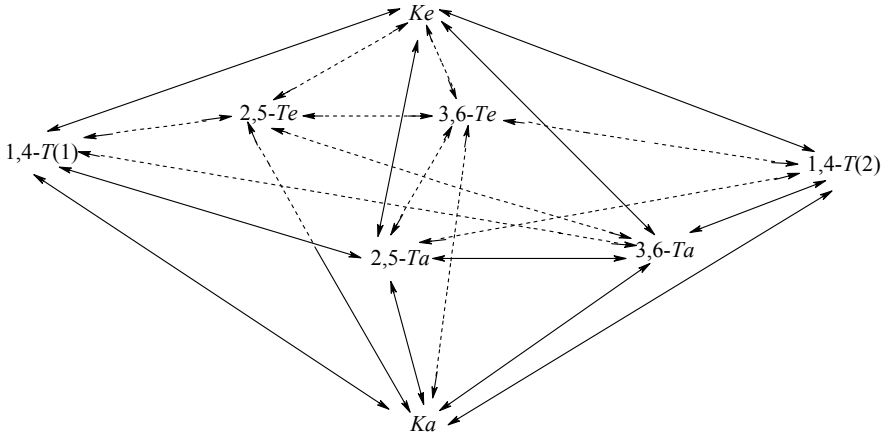


Table 1. Relative Energies of the Minima on the Potential Energy Surface of 4-Methyl-1,3-dioxane

Method	Δ*E*, kcal/mol*						
	Ka	2,5-*Te*	3,6-*Te*	1,4-*T*(1)	1,4-*T*(2)	3,6-*Ta*	2,5-*Ta*
MM^{+}*[2]	2.4	4.8(4)	4.4	4.8(2)	5.1	5.7	6.8
MM^{+}*[3]	2.8	4.7	4.5	8.8	5.4	5.8	6.7
STO-3G	2.6	4.4	4.9	5.0	5.4	5.9(7)	6.0(1)
3-21G	2.4	3.5	4.0	4.1(6)	4.5(1)	4.4(8)	4.2(0)
6-31G (d)	4.6	5.7	5.8	7.2	7.4	8.2	7.9
6-31G (d, p)	3.4	4.5	5.8	6.7	6.3	7.1	7.5

* Relative to form *Ke*.

*[2] In this regime dipole moments of bonds are calculated.

*[3] In this regime the partial charges on atoms are calculated.

Each conformational transition is carried out by a change in one of the intracyclic torsional angles. As a result it emerges that that the principal minimum on the potential energy surface corresponds to the form *Ke* and the closest local minimum corresponds to the form *Ka* (Table 1). Next on the energy scale are flexible forms in different orders according to the method of calculation. In individual cases, for example when using the MM^+, STO-3G, and 3-21G approximations, they are practically degenerate with respect to energy (differing by less than 0.1 kcal/mol). It should be noted that within the range of semiempirical aproximations (AM1, PM3, TNDO) not all the conformers of a given set are realized: separate flexible forms are missing.

The results obtained indicate that the potential energy surface has a more complex character in comparison with those of the unsubstituted dioxanes [2, 3, 6] and of 2-methyl-1,3-dioxane [4] as a result of the increased number of *twist*-conformers: 1,4-*T*(1) and 1,4-*T*(2), 3,6-*T*(*e*) and 3,6-*T*(*a*), and also 2,5-*Ta*. This arises because of the lower symmetry of the heterocyclic ring because of the presence of the substituent at the atom C-4.

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