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SHORT COMMUNICATIONS

Analysis of the Potential Energy Surface of 1,3-Dioxane and Its Protonated Form

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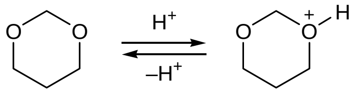
1,3-Dioxanes are practically important oxygen-containing heteroanalogs of cyclohexane. Protonation of these compounds, as well as of other 1,3- and 1,3,2-heterocycles, gives cyclic oxonium ions. The latter are formed as intermediates in numerous acid-catalyzed heterolytic reactions involving cyclic boron acid esters, 1,3-dioxa-2-silacyclohexanes, and cyclic acetals, which lead to formation of esters, 1,3-diols, and other valuable products of organic and petrochemical synthesis [1–4]. However, oxonium ions could be detected experimentally only at temperatures below –50°C, which strongly restricts the applicability of physical methods for studying fine details of their structure; therefore, such information is lacking in the literature. We thought it reasonable to examine the structure and conformational behavior of such species by quantum-chemical methods. The present communication reports on the results of comparative study of the potential energy surfaces (PES) of unsubstituted 1,3-dioxane (**I**) and its protonated form **II** in the gas phase in terms of the STO-3G and 6-31G** nonempirical methods. The calculations were performed using HyperChem software package [5].



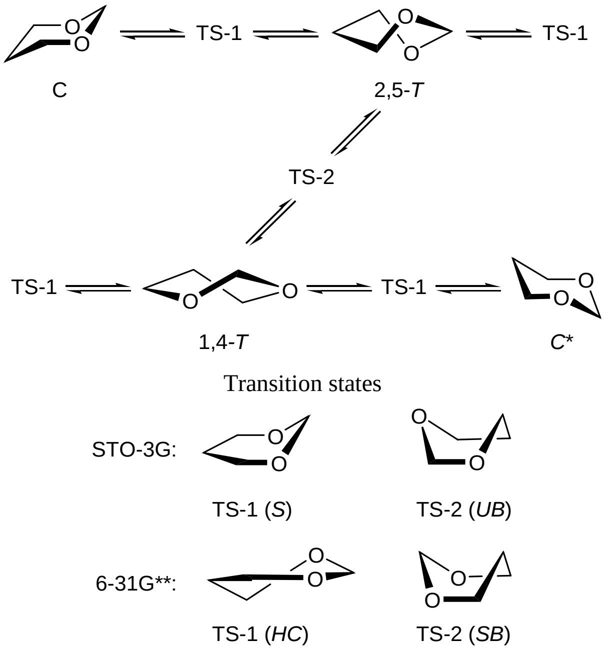
I **II**

According to published data, compound **I** in solution gives rise to fast (on the NMR time scale) ring inversion with a potential barrier $\Delta G^{\neq}$ of 9.7–10.1 kcal/mol [6]. We have found that the conformational isomerism $C \leftrightarrow C^*$ can take two pathways, each including (in addition to global minima corresponding to conformers *C* and *C** which are degenerate in energy) two local minima (flexible *twist* forms 2,5-*T* and 1,4-*T*) and two maxima [transition states TS-1 and TS-2 corresponding to *sofa* (*S*), *half-chair* (*HC*), *symmetric boat* (*SB*), and *unsymmetric boat* (*UB*) conformations; Table 1, Scheme 1) on the potential energy surface [7].

According to both calculation procedures, the population of 1,4-*T* is slightly greater. On the other hand, the two pathways pass through the same global maximum TS-1, and hence they are almost equally probable. This is confirmed by good agreement between the experimental ($\Delta G^{\neq}$) and theoretical ($\Delta E^{\neq}$, TS-1) barriers to inversion (9.7 and 9.3 kcal/mol, respectively).

Pathways of conformational isomerism of oxonium ion **II** (Scheme 2) include *chair* conformers with axial

Scheme 1.



(*Ca*) and equatorial (*Ce*) orientation of the proton on O^1 and also flexible conformers 1,4-*Ta* and 1,4-*Te*. The first of these (*Ca*) corresponds to the global minimum, and *Ce*, 1,4-*Ta*, and 1,4-*Te* occupy local minima on the PES; *sofa*, *half-chair*, and 3,6-*twist* conformers correspond to maxima on the PES (Table 2). Of the two pathways, the more favorable is *Ca*↔1,4-*Ta*↔*Ce* due to lower barrier to inversion (TS-2 against TS-1). The two calculation methods predict higher population of alternative *Ce* conformer, as compared to 1,4-*Ta* and 1,4-*Te*. On the other hand, the conformational equilibrium is appreciably displaced toward *Ca* conformer (Scheme 3). The fraction of *Ca* at 20°C should be no less than 95%.

Scheme 2.

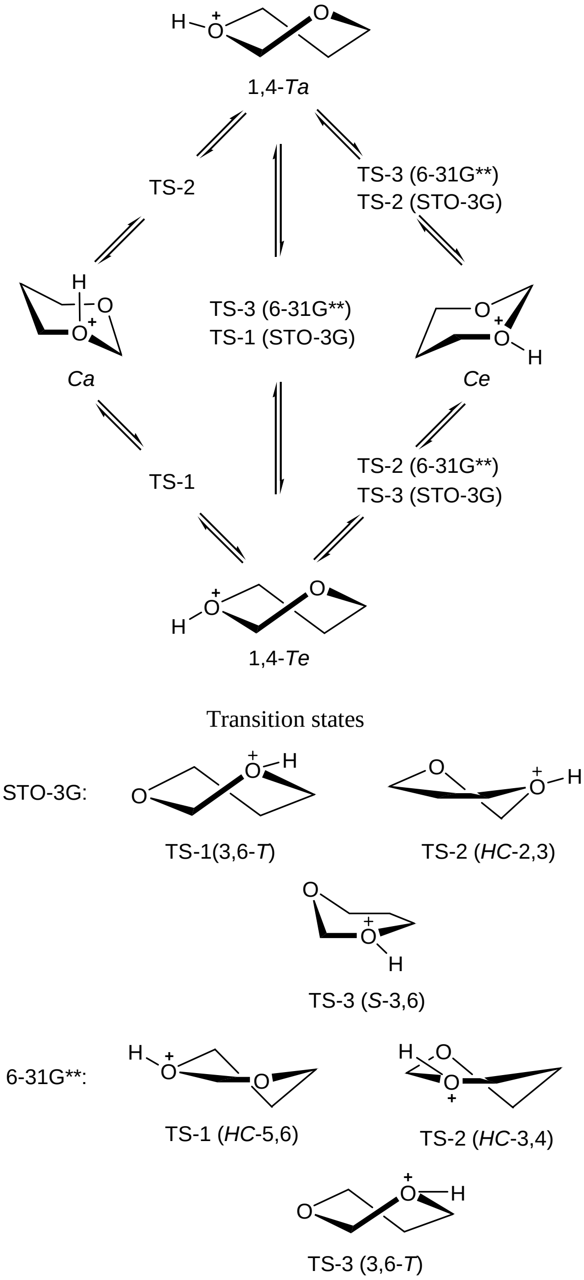


Table 1. Energy parameters of the inversion *C*↔*C** of 1,3-dioxane (kcal/mol)

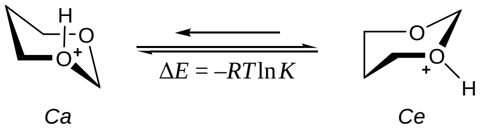
Method	Minima, ΔE^a		Maxima, $\Delta E^{\neq a}$	
	2,5-*T*	1,4-*T*	TS-1	TS-2
STO-3G	3.6	4.5	6.9	5.3
6-31G**	4.4	5.7	9.3	6.6

[a] Relative to *chair C* (*C**).

Table 2. Energy parameters of the *Ca*↔*Ce* inversion of oxonium ion **II** (kcal/mol)

Method	Minima, ΔE				Maxima, $\Delta E^{\neq}$		
	Ca	*Ce*	1,4-*Ta*	1,4-*Te*	TS-1	TS-2	TS-3
STO-3G	0	1.7	2.5	4.3	10.9	7.2	8.2
6-31G**	0	1.7	2.9	4.3	13.2	7.5	11.3

Scheme 3.



Also, we can state that the calculated barriers to the conformational *chair–chair* isomerization of 1,3-dioxane **I** are appreciably lower than those found for oxonium ion **II**: 6.9 and 10.9 kcal/mol (STO-3G) and 9.3 and 13.2 kcal/mol (6-31G**), respectively.

Thus our results indicate that protonation of one oxygen atom in the 1,3-dioxane molecule leads to appearance of an alternative nondegenerate *chair* conformer and considerably increases the barrier to inversion in the gas phase.

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