

SHORT  
COMMUNICATIONSSimulation of the Potential Energy Surface  
of 2-Methyl-1,3-dioxane

A. E. Kuramshina, S. A. Bochkor, and V. V. Kuznetsov

Ufa State Petroleum Technical University, ul. Kosmonavtov 1, Ufa, 450062 Bashkortostan, Russia  
e-mail: kuzmaggy@mail.ru

Received February 4, 2005

DOI: 10.1134/S1070428006040221

Interest in 1,3-dioxanes originates from specificity of their structure [1] and stimulates studies on the potential energy surfaces (PES) of their molecules by computer simulation. It was shown previously [2–5] that the PES of unsubstituted 1,3-dioxane, as well as of 4,4-dimethyl-1,3-dioxane, includes global (*chair* conformer) and local minima [1,4-*twist* (1,4-*T*) and 2,5-*twist* (2,5-*T*)] and maxima corresponding to *half-chair*, *sofa*, and *unsymmetrical boat* conformations. The present communications reports the results of our study on conformational transformations of 2-methyl-1,3-dioxane (**I**) in the gas phase on the Hartree–Fock level using semiempirical (AM1, PM3) and nonempirical (STO-3G, 6-31G\*\*) approximations. The calculations were performed using HyperChem software [6].

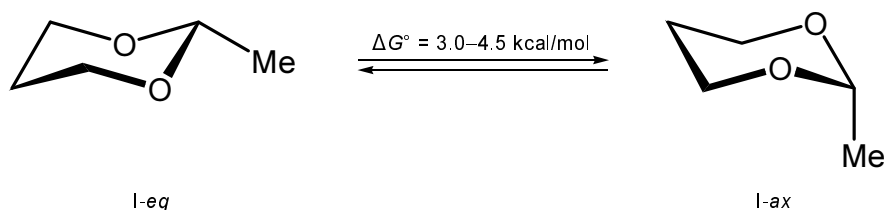
It is known that the global minimum on the PES of 1,3-dioxanes is occupied by the *chair* conformer with predominantly equatorial orientation of the alkyl substituent (**I-*eq***) (unlike conformer **I-*ax*** with the axial alkyl group). The <sup>1</sup>H NMR data unambiguously indicate that molecules **I** at room temperature exist mainly as conformers **I-*eq*** possessing a fairly high free conformational energy [7].

We have revealed the general pattern of conformational transformations and the characters of interme-

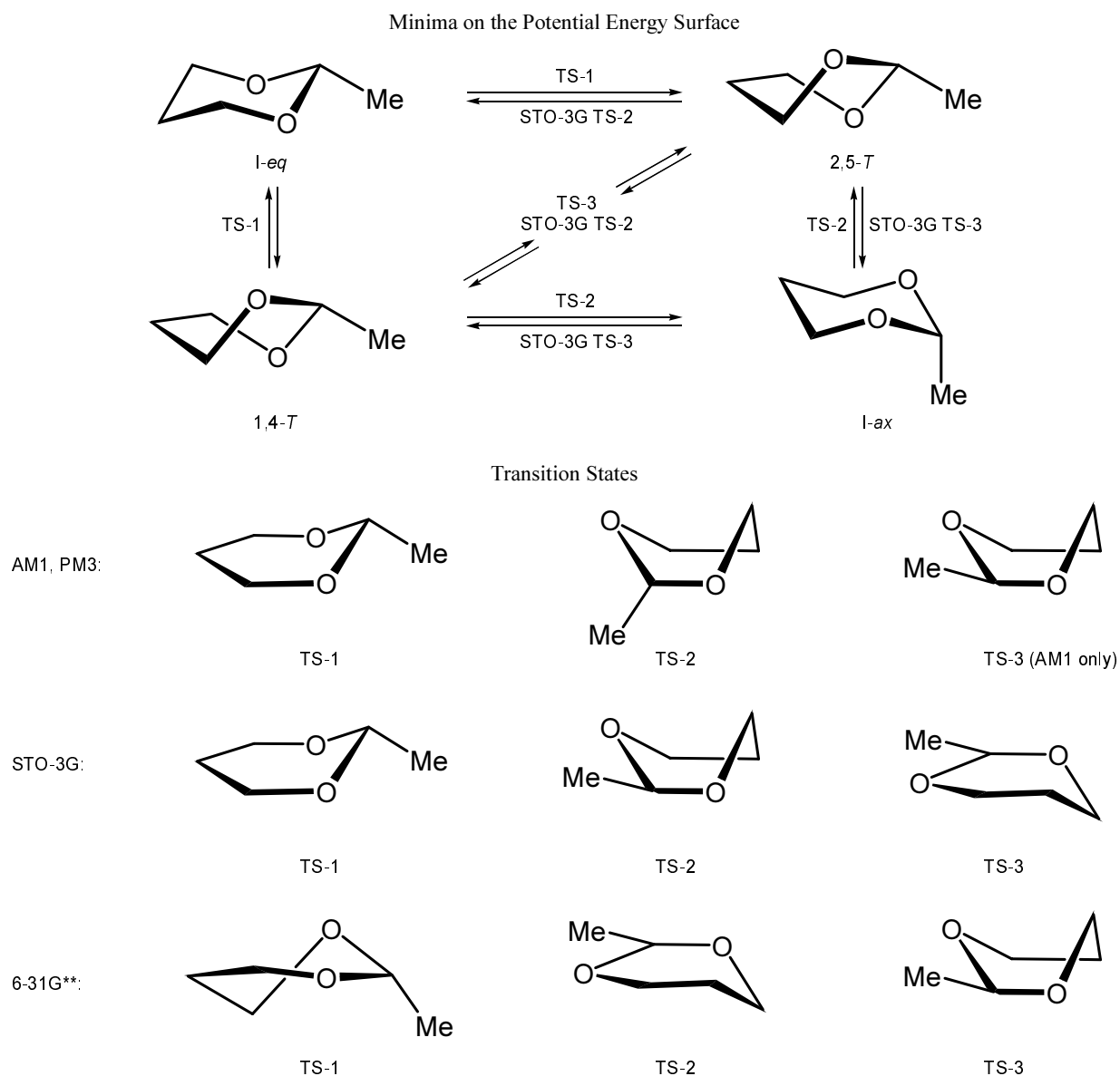
diat minima and transition states (TS) typical of 2-methyl-1,3-dioxane molecules (see table, Schemes 1, 2).

The results showed the existence of two pathways of conformational isomerization **I-*eq***  $\rightleftharpoons$  **I-*ax***, which are analogous to those observed for unsubstituted 1,3-dioxane and 4,4-dimethyl-1,3-dioxane [2–5] (PM3 calculations revealed only one pathway involving 2,5-*T* conformer). Conformers 1,4-*T* and 2,5-*T* are interconvertible through the TS-3 maximum (or TS-2 according to the STO-3G calculations). The global maximum on the PES is occupied by *sofa* conformer (AM1, PM3: TS-1; 6-31G\*\*: TS-2; STO-3G: TS-3). However, both pathways turned out to be almost equally probable. The results of 6-31G\*\* calculations satisfactorily reproduce the experimental difference in the energy between conformers **I-*eq*** and **I-*ax*** ( $\Delta G^\circ$  is  $4.07 \pm 0.46$  kcal/mol in favor of **I-*eq*** [7]). On the other hand, the experimental value of  $\Delta G^\ddagger$  for conformational isomerization of compound **I** is unknown; the  $\Delta E^\ddagger$  value 10.6 kcal/mol (TS-2, 6-31G\*\*) approaches the experimental barrier to inversion in unsubstituted 1,3-dioxane (9.0–10.1 kcal/mol [7]). It should also be noted that the global minimum calculated in the AM1 and PM3 approximation (conformer **I-*ax***) does not correspond to the experimental data, presumably

Scheme 1.



Scheme 2.

Energy parameters of the *I-eq*  $\rightleftharpoons$  *I-ax* inversion in 2-methyl-1,3-dioxane

| Method  | Minima, $\Delta E$ , kcal/mol |             |               |               | Maxima, $\Delta E^\ddagger$ , kcal/mol |      |      |
|---------|-------------------------------|-------------|---------------|---------------|--|------|------|
|         | <i>I-eq</i>                   | <i>I-ax</i> | 1,4- <i>T</i> | 2,5- <i>T</i> | TS-1                                   | TS-2 | TS-3 |
| AM1     | 0.3                           | 0           | 2.6           | 2.5           | 3.8                                    | 2.7  | 2.8  |
| PM3     | 1.6                           | 0           | –             | 3.4           | 3.4                                    | 5.0  | –    |
| STO-3G  | 0                             | 3.7         | 4.7           | 4.7           | 8.6                                    | 5.0  | 12.5 |
| 6-31G** | 0                             | 4.8         | 5.5           | 5.2           | 9.3                                    | 10.6 | 5.8  |

because of imperfect parameterization utilized in these procedure.

Thus, our data indicate greater conformational rigidity of 2-methyl-1,3-dioxane molecules as com-

pared to unsubstituted 1,3-dioxane and 4,4-dimethyl-substituted analog [2–5], which is determined by spatial interactions between the axial methyl group on  $C^2$  and hydrocarbon fragment of the ring.

## REFERENCES

1. Rakhmankulov, D.L., Karakhanov, R.A., Zlotskii, S.S., Kantor, E.A., Imashev, U.B., and Syrkin, A.M., *Itogi Nauki Tekh. Tekhnol. Org. Veshch.*, 1979, no. 5, p. 6.
2. Kuramshina, A.E., Bochkor, S.A., and Kuznetsov, V.V., *IV Vserossiiskaya nauchnaya internet-konferentsiya "Komp'yuternoe i matematicheskoe modelirovanie v estestvennykh i tekhnicheskikh naukakh"* (IVth All-Russia Scientific Internet Conf. "Computer and Mathematical Simulation in Natural and Technical Sciences"), Tambov, 2002, no. 18, p. 54.
3. Kuramshina, A.E., Bochkor, S.A., and Kuznetsov, V.V., *Bashkir. Khim. Zh.*, 2004, no. 11, p. 81.
4. Mazitova, E.G., Kuramshina, A.E., and Kuznetsov, V.V., *Russ. J. Org. Chem.*, 2004, vol. 40, p. 588.
5. Sarvarova, G.S., Kuramshina, A.E., Bochkor, S.A., and Kuznetsov, V.V., *Integratsiya nauki i vysshego obrazovaniya v oblasti organicheskoi i bioorganicheskoi khimii i mekhaniki mnogofaznykh sistem. Materialy II Vserossiiskoi nauchnoi internet-konferentsii* (Integration of Science and Higher Education in the Fields of Organic and Bioorganic Chemistry and Mechanics of Multiphase Systems. Proc. IInd All-Russia Scientific Internet Conf.), Ufa: Reaktiv, 2003, p. 137.
6. *HyperChem 5.02. Trial version.* [www.hyper.com](http://www.hyper.com).
7. *Internal Rotation in Molecules*, Orville-Thomas, W.J., Ed., London: Wiley, 1974.