

SHORT
COMMUNICATIONS

Conformational Transformations of 4-Methyl-1,3-dioxan-2-one

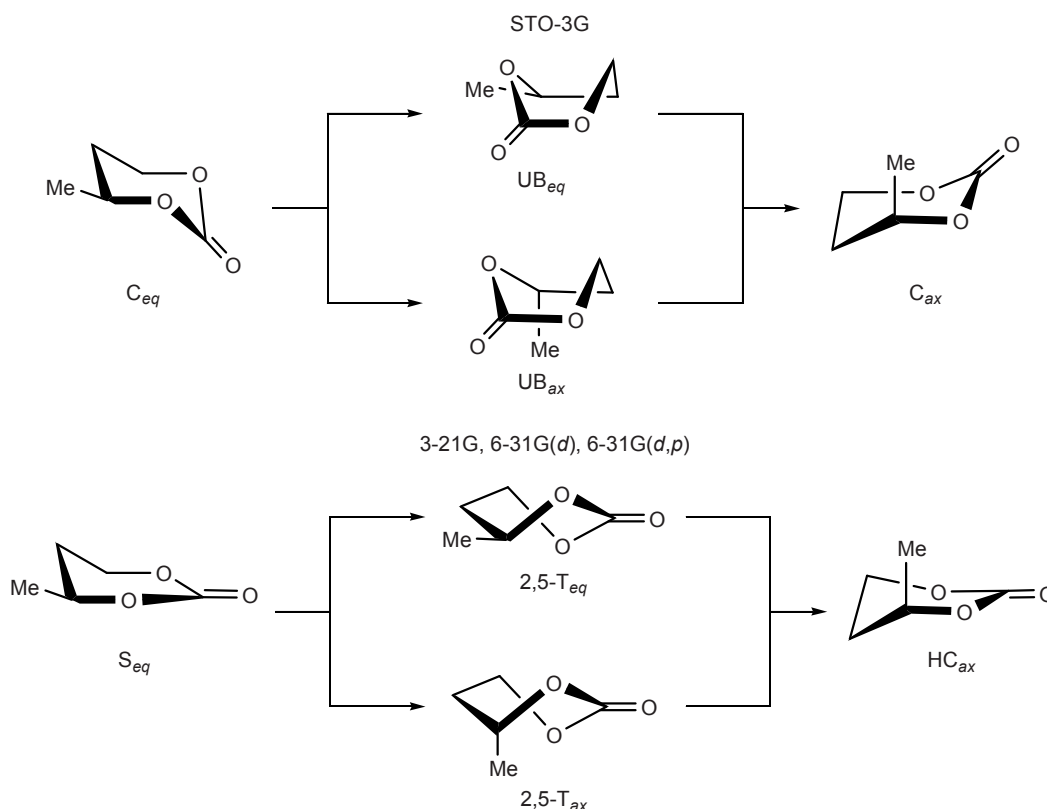
A. E. Kuramshina^a, S. A. Bochkor^a, and V. V. Kuznetsov^{a, b}^a Ufa State Petroleum and Technical University, ul. Kosmonavtov 1, Ufa, 450062 Bashkortostan, Russia
e-mail: kuz@anrb.ru^b Institute of Molecules and Crystals Physics, Ufa Research Center, Russian Academy of Sciences,
pr. Otyabrya 151, Ufa, 450075 Bashkortostan, Russia

Received July 16, 2008

DOI: 10.1134/S1070428009040253

Interest in cyclic carbonates is related to specificity of their structure and useful properties [1–7]. The presence of an sp^2 -hybridized carbon atom in the 2-position gives rise to considerably different stereochemical behavior of cyclic carbonates as compared to other 1,3-dioxanes. Estimation of this effect is an important problem in conformational analysis of six-membered saturated oxygen-containing heterocycles. For this purpose, approaches based on quantum-chemical calculations are quite appropriate. We previously showed [8]

by semiempirical quantum-chemical methods that the potential energy surface (PES) of 1,3-dioxan-2-one contains a minimum (energy-degenerate *sofa* conformation S) and a maximum (2,5-*twist* conformer 2,5-T). In the present study we examined conformational behavior of 4-methyl-1,3-dioxan-2-one (I) in the gas phase in terms of empirical (MM+) and nonempirical [RHF//STO-3G, 3-21G, 6-31G(*d*), 6-31G(*d,p*), and MP2//6-31G(*d,p*)] quantum-chemical approximations using HyperChem software package [9].



Energy minima and maxima on the potential energy surface of 4-methyl-1,3-dioxan-2-one (**I**) and minima on the potential energy surface of 4-methyl-1,3-dioxane (**II**) (kcal/mol)

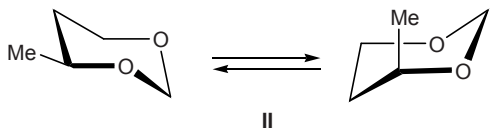
| Method | $\Delta E_{\text{I}}^{\text{a}}$ | $\Delta E_{\text{II}}^{\text{a}}$ | $\Delta E_{\text{I}}^{\text{b}}$ | $\Delta \Delta E_{\text{I}}^{\text{c}}$ |
|--------------------------|----------------------------------|-----------------------------------|----------------------------------|---|
| MM+ ^b | 0.8 | 2.4 | – | – |
| MM+ ^c | 1.1 | 2.8 | – | – |
| RHF//STO-3G | 1.3 | 2.6 | 2.0–3.4 | 1.4 |
| RHF//3-21G | 0.8 | 2.4 | 1.1–1.5 | 0.4 |
| RHF//6-31G(<i>d</i>) | 1.6 | 4.6 | 2.2–3.9 | 1.7 |
| RHF//6-31G(<i>d,p</i>) | 1.7 | 3.4 | 2.2–3.9 | 1.7 |
| MP2//6-31G(<i>d,p</i>) | 1.4 | 3.4 | 2.0–3.5 | 1.5 |

^a Relative to the energy of the equatorial conformer.

^b With account taken of bond dipole moments.

^c With account taken of partial charges on atoms.

We found that, depending on the calculation method, minimum on the PES of compound **I** is occupied by *chair* (C_{eq} , STO-3G) or *sofa* conformer (S_{eq} , all other methods) with equatorial methyl substituent (see table). The second minimum corresponds to *chair* (C_{ax} , STO-3G) or *half-chair* conformer (HC_{ax} , all other approximations) with axial methyl group. The difference between the energy minima (ΔE) ranges from 0.8 to 1.6 kcal/mol, i.e., it is smaller than the corresponding difference for 4-methyl-1,3-dioxane (**II**) by a factor of 2–3 (see table).



It is known that, unlike 2-oxo analog, potential energy surfaces for 1,3-dioxanes imply two-step transition from equatorial to axial *chair* conformer and contain additional intermediate minima which correspond to 1,4- and 2,5-*twist* structures [8, 10]. Thus introduction of an oxo group into the 2-position considerably reduces the ΔE value. Nevertheless, the calculated energy differences between conformers of **I** suggest that the contribution of the axial conformers should be

insignificant, which is confirmed by experimental data [7]. On the other hand, the calculated activation barrier (ΔE^{\ddagger}) to conformational transformation of molecule **I** is 2–3 times lower than that calculated for unsubstituted 1,3-dioxane in terms of the same approximation [10]. Furthermore, the PES of cyclic carbonate **I**, as well as PESs of 4-substituted 1,3,2-dioxaborinanes [11], contain two maxima occupied by *unsymmetrical boat* conformers HB_{eq} and HB_{ax} (STO-3G) or 2,5-*twist* conformers 2,5- T_{eq} and 2,5- T_{ax} (other methods); the corresponding energy differences ($\Delta \Delta E^{\ddagger}$) range from 0.4 to 1.7 kcal/mol.

The above results indicate higher conformational mobility of six-membered cyclic carbonates in comparison to 1,3-dioxanes due mainly to the lack of additional steric interactions in the heteroatom fragment of the ring.

REFERENCES

- Carothers, W.H. and Van Natta, F.J., *J. Am. Chem. Soc.*, 1930, vol. 52, p. 314.
- Pattison, D.B., *J. Am. Chem. Soc.*, 1957, vol. 79, p. 3455.
- Wang, I., Britt, C.O., and Boggs, J.E., *J. Am. Chem. Soc.*, 1965, vol. 87, p. 4950.
- Shuikin, I.I., Bartok, M., and Kozma, B., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, p. 153.
- Pihlaja, K. and Rossi, K., *Acta Chem. Scand., Ser. B*, 1977, vol. 31, p. 899.
- Pihlaja, K., Teinonen, K.-J., and Äyräs, P., *Suom. Kem. B*, 1970, vol. 43, p. 41.
- Pihlaja, K. and Rossi, K., *Acta Chem. Scand., Ser. B*, 1983, vol. 37, p. 289.
- Kuramshina, A.E., Bochkor, S.A., and Kuznetsov, V.V., *Sovrem. Naukoem. Tekhnol.*, 2006, no. 2, p. 82.
- HyperChem 7.01. Trial version. www.hyper.com.*
- Mazitova, E.G., Kuramshina, A.E., and Kuznetsov, V.V., *Russ. J. Org. Chem.*, 2004, vol. 40, p. 588.
- Valiakhmetova, O.Yu., Bochkor, S.A., and Kuznetsov, V.V., *Sovrem. Naukoem. Tekhnol.*, 2008, no. 2, p. 140.