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Conformational Analysis of Six-Membered Cyclic Carbonates

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Abstract—The conformational isomerization of 2-oxo-1,3-dioxane and its methyl analogs was investigated by means of ab initio RHF//6-31G(d,p) and MP2//6-31G(d,p) quantum-chemical methods. It is shown that in comparison with 1,3-dioxanes the potential energy surface of the mentioned compounds has a fewer number of stationary points and includes two minima corresponding to conformers of *sofa* or *distorted sofa* configuration and one maximum corresponding to 2,5-*twist* form. The value of potential barrier of interconversion of cyclic carbonates is significantly lower than that of the analogously substituted 1,3-dioxanes.

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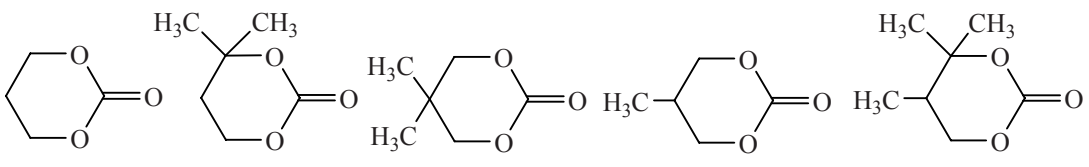
The interest in cyclic carbonates originates from their structural features and a complex of practically useful properties [1–7]. The presence of sp^2 carbon atom in the second position of the ring causes essential differences in stereochemistry of the molecules of such substances compared to other 1,3-dioxacycloalkanes. The proper estimate of influence of the carbon atom valence state on a stereodynamic behavior of the molecules of cyclic hydrocarbon heteroanalogs is an actual problem of conformational analysis [8, 9]. A promising way of its solution consists in a computer simulation of the conformational isomerization. It was shown earlier [10–14] that potential energy surface (PES) of the symmetrically substituted 1,3-dioxanes studied by means of semiempirical and nonempirical quantum-chemical approaches contained *chair* conformers as the minima and also 1,4- and 2,5-*twist* forms, therewith the isomerization of one *chair* conformer into another proceeds by two routes. By the data of semiempirical calculations PES of 2-oxo-1,3-dioxane includes energetically degenerated *sofa* (*S*) forms and a maximum corresponding to 2,5-*twist* form (2,5-*T*) [15]. This work consists in the study of isomerization pathways of 2-oxo-1,3-dioxane and its methyl-substituted analogs **I–V** by means of RHF//6-31G(d,p) and MP2//6-31G(d,p) nonempirical quantum-chemical approaches using HyperChem package [16] under conditions simulating behavior of these molecules in the gas phase (Scheme 1).

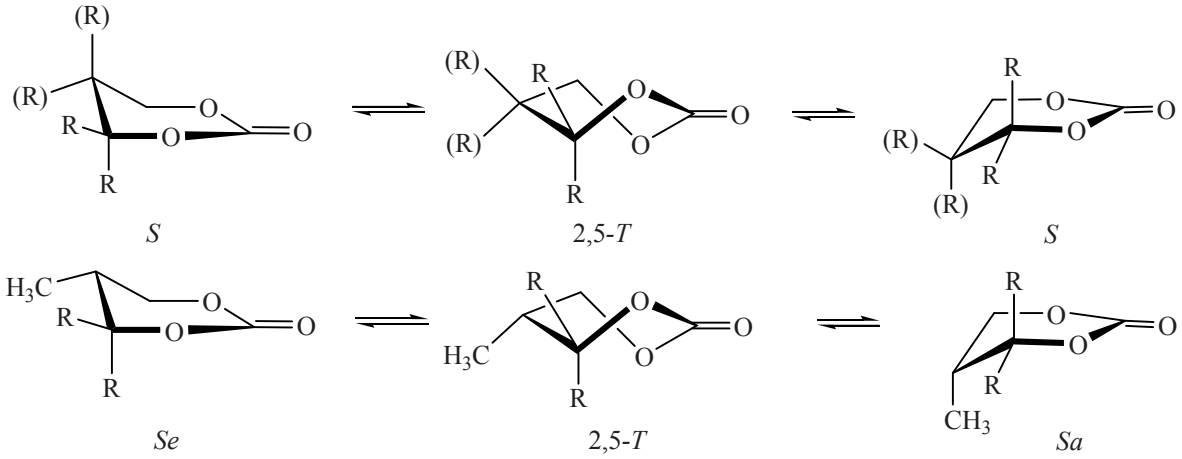
Conformational analysis is known [8] to include the study of minima and barriers between them. We established that PES of compounds **I–V** contain two minima, equatorial and axial *sofa* conformers *Se* and *Sa* (energetically degenerated in the case of carbonates **I–III** and slightly twisted in the case of compounds **II**

Scheme 1.



I **II** **III** **IV** **V**

Scheme 2.

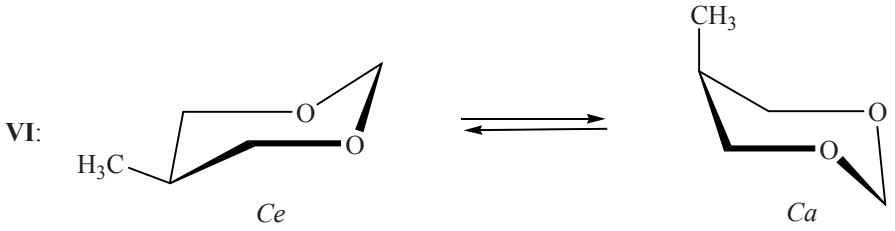


I–III: R = H, CH_3; **IV, V**: R = H, CH_3.

and **V**), and also a transition state corresponding to 2,5-*T*-form (Scheme 2).

Low values of activation barriers to the conformational isomerization for all the studied compounds primarily have engaged our attention. They almost do not depend on the number or position of methyl substituents in the ring. These values are more than 3–4 times lower than the value $\Delta E^{\neq}$ for the unsubstituted 1,3-dioxane [9.3 and 6.6 kcal mol^{-1} , RHF//6-31G(d,p)] [11], and they also are 4–5 times lower than the calculated activation barriers of the model 5-methyl-1,3-dioxane **VI** studied in this work (see table, Scheme 3).

Scheme 3.



Calculated parameters of conformational isomerization for compounds **I–VI** (kcal mol^{-1})

Comp. no.	Parameters	RHF//6-31G(d,p)	MP2//6-31G(d,p)
I	ΔE	0	0
	$\Delta E^{\neq}$	2.0	1.8
II	ΔE	0	0
	$\Delta E^{\neq}$	2.2	2.2
III	ΔE	0	0
	$\Delta E^{\neq}$	2.3	2.3
IV	ΔE	0.9	0.3
	$\Delta E^{\neq}$	2.5	2.0
V	ΔE	1.4	0.9
	$\Delta E^{\neq}$	3.2	2.8
VI	ΔE	0.7	0.04
	$\Delta E^{\neq}$	10.4, 9.3, 6.2	11.6, 11.0, 7.0

Experimental values of $\Delta G^{\neq}$ for cyclic carbonates are not known. It is however presumable that they should be lower than those of the similarly substituted 1,3-dioxanes: The substitution of the sp^3-carbon by the trigonal sp^2-boron atom leads to an increase in the interconversion barrier of six-membered cyclic esters of boric acids, 1,3,2-dioxaborinanes, by 2–3 kcal mol^{-1} on the average [17, 18].

Differences in the energy values of conformers *Se* and *Sa* (ΔE) of carbonates **IV** and **V**, and also of dioxane forms *Ce* and *Ca* **VI** are insignificant. However, it should be admitted that the data of MP2//6-31G(d,p) method are erroneous: The experimental $-\Delta G^0$ values for methyl substituent at C-5 atom of the ring lie in the range 0.8–1.05 kcal mol^{-1} for 1,3-dioxanes [19] and 0.7–1.05 kcal mol^{-1} for

cyclic carbonates [6, 7]. In this connection it is interesting to estimate the value ΔG^0 for compounds **IV** and **V** by independent method using experimental (from ^{1}H NMR spectrum: $^3J_{AX}$, $^3J_{BX}$ [7]) and theoretical (J_{Aa}, J_{Ba}, J_{Ae}, J_{Be}) vicinal spin-spin coupling constants of conformers *Se* and *Sa* with the relative content of N and 1–N respectively [20]:

$$^3J_{AX} + {}^3J_{BX} = N(J_{Aa} + J_{Ba}) + (1 - N)(J_{Ae} + J_{Be}),$$
$$\Delta G^0 = -RT \ln [N/(1 - N)].$$

In its turn the theoretical coupling constants can be determined by the modified Karplus equation [21] using torsion angles between the corresponding protons in conformers, which are participating in the binary equilibrium (optimal geometry data). Value of N calculated by us for carbonate **IV** is equal to 74, that is, the ratio of equatorial and axial conformers is 74:26 (76:24 by ^{13}C NMR data [7]), and value of ΔG^0 for methyl substituent is equal to ≈ –0.6 kcal mol^{-1} at 298 K. For carbonate **V** the ratio of equatorial and axial forms in mixture constitutes 86:14 (88:12 by [7]), and ΔG^0_{298} ≈ –1.1 kcal mol^{-1}. Most likely in the last case the increased ΔG^0 value is caused by steric interactions of substituents in the carbon fragment of the cycle.

Results obtained show that the conformational flexibility of cyclic carbonate molecules is higher compared with 1,3-dioxanes. It is due to a decrease in the number of the nonbonded interactions in the heteroatomic part of ring.

EXPERIMENTAL

Carbonates **I–V** and their structural and also their conformational parameters were described in [6, 7], and the corresponding properties of dioxanes **VI** were reported in monograph [19]. The route and values of interconversion barriers were determined by HyperChem package [16].

The PSE stationary points were attributed to maxima (form 2,5-*T*) due to was confirmed by the presence of one negative frequency in the corresponding Hesse matrix. Applicability of calculation methods to determine values of free energy for substituents in 1,3-dioxanes was discussed in [22]. The modified Karplus equation is represented as [21]:

$$^3J_{HH} = P_1\cos^2\varphi + P_2\cos\varphi + P_3 + \sum\Delta\chi_i[P_4 + P_5\cos^2(\xi_i\varphi + P_6|\Delta\chi_i|)],$$

where $\Delta\chi_i$ is electronegativity difference between substituents of the corresponding ethane fragment and hydrogen, φ is the calculated torsion angles between interacting protons, ξ_i takes the values ±1 depending on orientation of substituents at the carbon atoms of the ethane fragment, and P_1–P_6 are parameters depending on the substitution degree of this fragment. On solving this equation the numerical values of parameters P_1–P_6 (P_1 = 13.22, P_2 = –0.99, P_3 = 0, P_4 = 0.87, P_5 = –2.46, P_6 = 19.9°) were used for fragment containing three substituents, and electronegativity values from [23] were used. The numerical values of experimental coupling constants are equal to: $^3J_{AX}$=9.2, $^3J_{BX}$ = 4.5 and $^3J_{AX}$ = 10.85, $^3J_{BX}$ = 5.0 Hz for cyclic carbonates **IV** and **V,** respectively [7].

REFERENCES

1. Carothers, W.H. and Van Natta, F.J., *J. Am. Chem. Soc*., 1930, vol. 52, no. 1, p. 314.
2. Pattison, D.B., *J. Am. Chem. Soc*., 1957, vol. 79, no. 7, p. 3455.
3. Wang, I., Britt, C.O., and Boggs, J.E., *J. Am. Chem. Soc*., 1965, vol. 81, no. 21, p. 4950.
4. Shujkin, I.I., Bartok, M., and Kozma, B., *Izv. Akad. Nauk SSSR Ser. Khim*., 1967, no. 1, p. 153.
5. Pihlaja, K. and Rossi, K., *Acta Chem. Scand*., 1977, vol. 31, no. 10, p. 899.
6. Pihlaja, K., Teinonen, K-J., and Äyräs, P., *Suomen Kemistilelehti*, 1970, vol. 43, no. 1, p. 41.
7. Pihlaja, K. and Rossi, K., *Acta Chem. Scand*., 1983, vol. 37, no. 4, p. 289.
8. Dashevskii, V.G., *Konformatsii organicheskikh molekul* (Conformations of Organic Molecules), Moscow: Khimiya, 1974, p. 432.
9. Stoddart, J., *Stereokhimiya uglevodov* (Carbohydrates Stereochemistry), Moscow: Mir, 1975, p. 304.
10. Freeman, F. and Uyen Do, K., *J. Mol. Struct. (Theochem),* 2002, vol. 577, no. 1, p. 43.
11. Mazitova, E.G., Kuramshina, A.E., and Kuznetsov, V.V., *Zh. Org. Khim*., 2004, vol. 40, no. 4, p. 615.
12. Kuramshina, A.E., Bochkor, S.A., and Kuznetsov, V.V., *Zh. Org. Khim*., 2006, vol. 42, no. 4, p. 629.
13. Kuramshina, A.E., Tseplin, E.E., Bochkor, S.A., Khvostenko, O.G., and Kuznetsov, V.V., *Fizika v Bashkortostane* (Physics in Bashkortostan), Ufa: Gilem, 2005, no. 3, p. 161.
14. Mamleev, A.Kh., Gunderova, L.N., Galleev, R.V., Shapkin, A.A., Faizullin, M.G., Gorbunova, N.V., Shornikov, D.V., and Kantor, E.A., *Zh. Strukt. Khim*., 2007, vol. 48, no. 3, p. 501.
15. Kuramshina, A.E., Bochkor, S.A., and Kuznetsov, V.V., *Sovremennye naukoyomkiye tekhnologii* (Actual High Technology), 2006, no. 2, p. 82.

16. *HyperChem 7.01. Trial version. www.hyper.com*.

17. Carton, D., Pontier, A., Ponet, M., Soulie, J., and Cadiot, P., *Tetrahedron Lett*., 1975, no. 28, p. 2333.

18. Kuznetsov, V.V., Valiakhmetova, O.Yu., and Bochkor, S.A., *Khim. Geterotsikl. Soed*., 2007, no. 12, p. 1860.

19. *Vnutrennee vrashchenie molekul Molecules Internal Rotation*, Orwill-Tomas, W.J., Ed., Moscow: Mir, 1975, p. 355.

20. Zefirov, N.S., Blagoveshchenskii, V.S., Kazimirchik, I.V., and Yakovleva, O.P., *Zh. Org. Khim*., 1971, vol. 7, no. 3, p. 594.

21. Haasnoot, C.A.G., de Leeuw, F.A.A.M., and Altona, C., *Tetrahedron*, 1980, vol. 36, no. 19, p. 2783.

22. Kuznetsov, V.V. and Alekseeva, E.A., *Khim. Geterotsikl. Soed*., 2003, no. 6, p. 839.

23. Huggins, M.L., *J. Am. Chem. Soc*., 1953, vol. 75, no. 17, p. 4123.