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## LETTERS TO THE EDITOR

# Conformational Transformations of Perhydro-1,3,2-dioxazine

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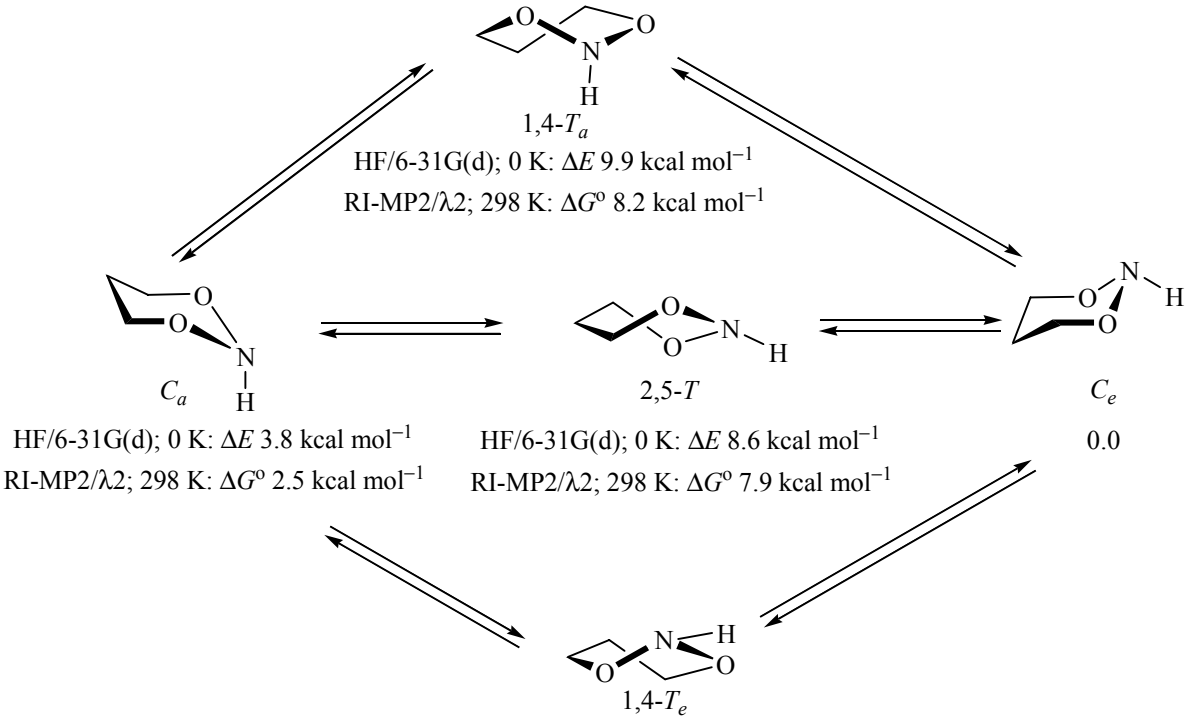
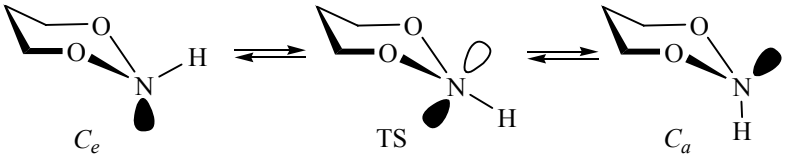
The interest in structural studies of perhydro-1,3,2-dioxazines, saturated heteroanalogs of cyclohexane containing O–N–O moiety in the ring, is associated with the structural features largely defined by the high configurational stability of the nitrogen atom [1–5]. Perhydro-1,3,2-dioxazine was synthesized more than 25 years ago [4]. However, the conformational conversion of compounds of this class until the present time remained unexplored. In this report the conformational isomerization of the unsubstituted perhydro-1,3,2-dioxazine was first studied using an *ab initio* HF/6-31G(d) approach within HyperChem package [6] and MR2-RI/λ2 method (PRIRODA package [7]).

The potential energy surface of the examined compound was found to contain several minima corresponding to the equatorial and axial *chair* conformers and flexible forms of 1,4- and 2,5-*twist* ($C_e$, $C_a$, 1,4-$T_e$, 1,4-$T_a$ and 2,5-$T$). The main minimum corresponds to the $C_e$ form within both the approximations. The $C_a$, 1,4-$T_e$, 1,4- $T_a$ and 2,5-$T$ forms are in order of decreasing of the relative stability.



The conformational isomerization $C_a \leftrightarrow C_e$ may be also due to the pyramidal inversion of the nitrogen atom. It occurs through a transition state (TS) corresponding to the planar configuration of this atom.




HF/6-31G(d); 0 K: $\Delta E^{\neq}$ 24.5 kcal mol$^{-1}$
RI-MP2/λ2; 298 K: $\Delta G^{\neq}$ 23.3 kcal mol$^{-1}$

Note that the calculated value of the potential barrier of this process ($\Delta E^{\neq}$, $\Delta G^{\neq}$) is close to the experimental data for acyclic *N*,*N*-dialkoxyamines (21.7–24.6 kcal mol$^{-1}$) [8] and confirms the high stability of the configuration of the nitrogen atom in compounds of this class.

The results show that the molecule of perhydro-1,3,2-dioxazine has a conformationally rigid structure, and the $C_e$ form is dominat in the equilibrium at room temperature.

## REFERENCES

1. Shtamburg, V.G., Rudchenko, V.F., Pleshkova, A.P., Chervin, I.I., and Kostyanovskii, R.G., *Izv. Akad. Nauk, Ser. Khim.*, 1980, no. 11, p. 2669.
2. Rudchenko, V.F., Shtamburg, V.G., Pleshkova, A.P., Nasibov, Sh.S., Chervin, I.I., and Kostyanovskii, R.G., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, no. 11, p. 2539.
3. Zolotoi, A.B., Dyachenko, O.A., Chervin, I.I., Rudchenko, V.F., Atovmyan, L.O., and Kostyanovskii, R.G., *Khim. Geterotsikl. Soed.*, 1983, no. 10, p. 1341.
4. Rudchenko, V.F., Shevchenko, V.I., and Kostyanovskii, R.G., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, no. 7, p. 1685.
5. Rudchenko, V.F., Shevchenko, V.I., and Kostyanovskii, R.G., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, no. 7, p. 1556.
6. *HyperChem 8.0. http://www.hyper.com.*
7. Laikov, D.N. and Ustynyuk, Yu.A., *Izv. Akad. Nauk, Ser. Khim.*, 2005, no. 3, p. 804.
8. Kostyanovsky, R.G., Rudchenko, V.F., Shtamburg, V.G., Chervin, I.I., and Nasibov, S.S., *Tetrahedron*, 1981, vol. 37, no. 24, p. 4245.