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LETTERS TO THE EDITOR

On the Degenerate Tautomerism

S. G. Semenov and M. V. Makarova

St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia
e-mail: mcmury@yandex.ru

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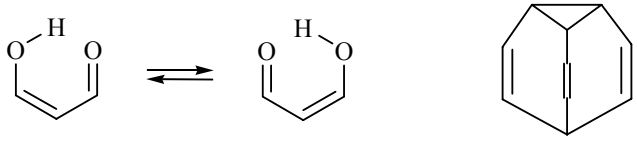
Tautomerism is a phenomenon of dynamic equilibrium between structural isomers (tautomers). This type of isomerism is characterized by fast reversible spontaneous interconversion of structural isomers. This interconversion is facilitated by low or permeable energy barriers between the molecule energy minima. Under the conditions of thermodynamic equilibrium, tautomers co-exist in comparable concentrations if their energy difference is low enough. If the energy difference is zero, tautomerism is referred to as a degenerate tautomerism [1].

The migration of a mobile hydrogen atom between the oxygen atoms of unsymmetrical intramolecular hydrogen bond in *cis*-enol of malonic dialdehyde (3-hydroxyprop-2-en-1-al **I**) is a common example of the degenerate prototropic tautomerism [1]. The co-existence of (10!/3) = 1209600 tautomers of bullvalene **II** is commonly known as an example of the degenerate valence tautomerism [2].[1] It should be noted however that such intramolecular reactions result in the rotation of molecule as a whole rather than in the interconversion of its structural isomers [3].

Both hydrogen shift in **I** and the Cope rearrangement of **II** in combination with certain molecule rotations are in fact symmetry operations, leaving the equilibrium nuclear configuration of the molecule intact.[2]



I **II**

At low temperatures, the symmetry of **II** is C_{3v}, whereas above 100°C all ^{1}H in the molecule are magnetically equivalent [2]. Such highly symmetric mixed state with equal average distances between any pair of the ten hydrogen atoms and equal average distances between any pair of the ten carbon atoms evidently does not correspond to symmetry of any polyhedron (the only polyhedron with equal distances between the vertices in 3D space is tetrahedron) and should therefore be described by a density matrix.

The intramolecular reaction product could be distinguished from the initial molecule in the case of partial isotopic substitution of the atoms (H → D, $^{12}C \rightarrow {}^{13}C$, $^{16}O \rightarrow {}^{17}O$ or ^{18}O) in **I** or in the case of bullvalene partial deuteration. However, such isotope-substituted tautomers are no longer degenerate due to the difference in the zero point energy. For example, **I**-1-^{18}O possesses by 0.008 kcal/mol less energy than **I**-3-^{18}O, and **I**-3-*d*, by 0.094 kcal/mol less than **I**-1-*d*. Even in the case of substitution of a stable nucleus with a metastable (excited) nucleus of the same mass, the tautomerism should be referred to as quasi-degenerate one, due to the electron-nuclear interaction, in particular, the commonly neglected

[1] Non-steric CH bonds in **I**, **II**, **IV**, and **V** structures are not shown.

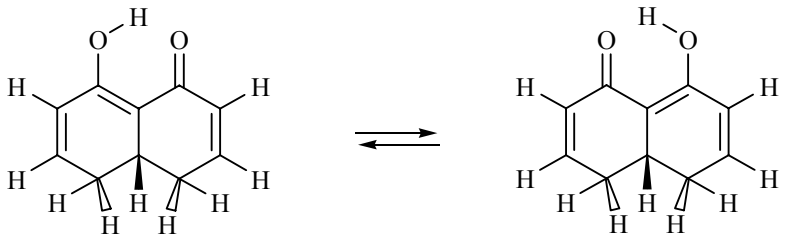
[2] Separately, these operations are not true symmetry operations (like, for example, the rotation by 360°/*n* around C_n or reflection with respect to the orthogonal plane in S_n, group).

interaction of the electron shell with the nucleus spin and quadrupole moment, changed upon excitation.

The true degenerate tautomerism is possible in the case of chiral tautomers (optical isomers). The enantiomers of (±)-8-oxo-4,4a,5,8-tetrahydronaphth-1-ol **III** can serve as an example (of degenerate tautomerism). We have studied the structure of this molecule using DFT M06-2X/cc-pVTZ quantum chemical method [4].

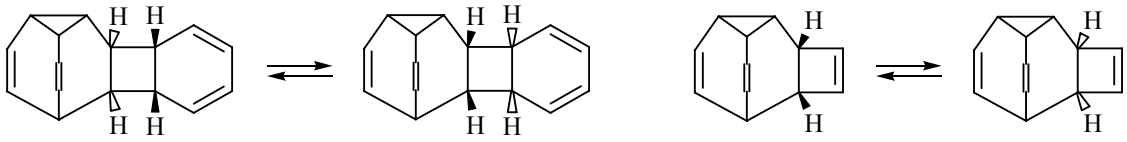
The equilibrium internuclear distances in hydroxypropenal fragments of **III** were as follows: 1.366 (C=C), 1.442 (C–C), 1.240 (C=O), 1.321 (C–O), 0.999 (O–H), 1.630 (O···H), and 2.536 (O···O) Å. In the structural formulas of (±)-**III**, we have depicted the carbon-hydrogen bond of the C^{4a} chiral center, which was almost antiparallel to the axial bonds of the significantly asymmetric C^4 and C^5 atoms. The calculated vibration spectra contained only real wavenumbers, $\nu \geq 109$ cm^{-1}. The absorption band at 3107 cm^{-1} was assigned to the O–H stretching vibration. The spectrum of the transition state contained a single imaginary wavenumber $\boldsymbol{i}1198$ cm^{-1}.

The (+) and (–) signs were assigned to the enantiomers of (±)-**III** basing on the calculated specific rotation of the plane polarized light at 589 nm, $[\alpha]_D = \pm 156°$. The energy barrier $E_{\cap}$ 0.3 kcal/mol was calculated taking into account ZPE for the energy of zero oscillations.



(+)-**III** (–)-**III**

The racemization of (±)-**IV** [5] or (±)-**V** hydrocarbons can serve as an example of the true degenerate valence tautomerism. The computed values of $[\alpha]_D$, were ±51 and ±172° and estimated energy barriers $E_{\cap}$ were 12.6 and 12.2 kcal/mol in the cases of (±)-**IV** and (±)-**V**, respectively.



(+)-**IV** (–)-**IV** (+)-**V** (–)-**V**

The computations were performed by means of the M06-2X/cc-pVTZ method with GAUSSIAN-09 software [6] at the Computational Center of St-Petersburg State University (http://cc.spbu.ru).

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