ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 8, pp. 1626–1627. © Pleiades Publishing, Ltd., 2013.
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LETTERS TO THE EDITOR

A Possibility of Oscillations of Equilibrium Bond Lengths in Cyclohexa-1,3,5-triene Derivatives

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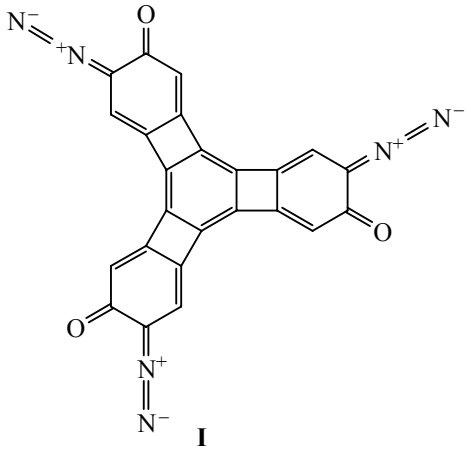
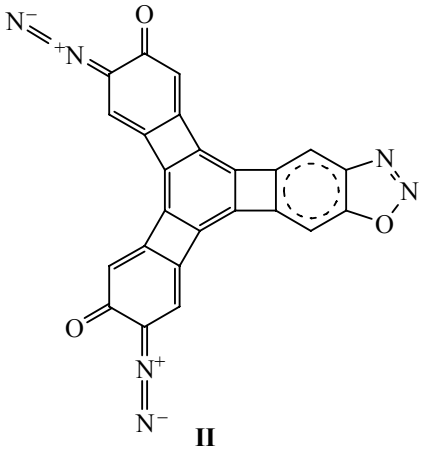
Received June 13, 2013

DOI: 10.1134/S1070363213080276

In continuation of quantum-chemical investigation of the cyclohexa-1,3,5-triene derivatives [1], in the present work we calculated the equilibrium structural parameters of the hypothetical molecules **I–IV** by M06-2X/cc-pVTZ method using the program GAUSSIAN-09 [2]. Vibrational spectra of all four isomers contain only real frequencies. The calculated energy of compounds **I–IV** are close enough for their co-existence as tautomers. Unlike Kekule who has assumed the reciprocal reversible conversion of the C=C and C–C bonds in the benzene molecule, we are discussing the possibility of reversible conversion of double and ordinary cyclohexa-1,3,5-triene bonds into the sesquialteral bonds.



I



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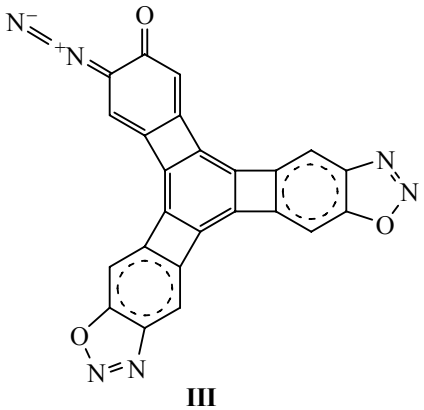

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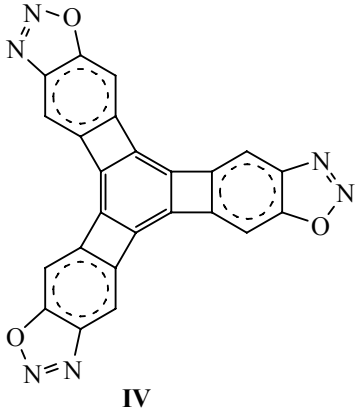
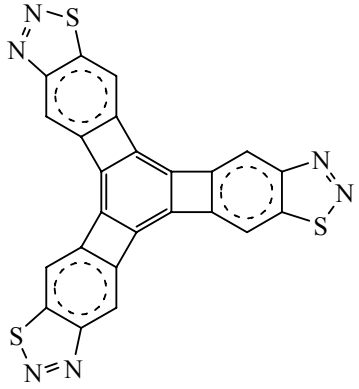


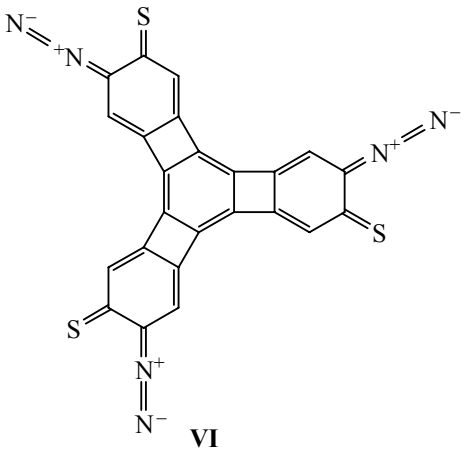
IV

Successive formation of one, two, and three 1,2,3-oxadiazole rings in the tris-α-diazocarbonyl compound **I** involves an increase in the energy by 3.1, 2.6, and 1.7 kcal mol^{-1}. In this case, the equilibrium lengths of three relatively short bonds of the central ring decrease (1.360 → 1.353 → 1.347 → 1.342 Å), and the lengths of three relatively long bonds increase (1.448 → 1.455 → 1.463 → 1.470 Å). In tautomer **IV** (with relative energy of 7.4 kcal mol^{-1}) there is distinct cyclohexa-1,3,5-triene structure with a difference in equilibrium lengths of 0.128 Å. In benzoid tautomer **I** the bond alternation is less (0.088 Å).

The substitution of the oxygen atoms by sulfur atoms stabilizes heterocycles in isomer **V** with cyclohexa-1,3,5-triene bonds C=C 1.343 Å and C–C 1.468 Å. The energy of isomer **VI** is higher by 65 kcal mol^{-1}. The content of the tautomers with open rings due to their high energy is negligible.

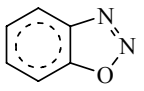


V

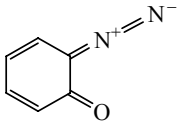


VI

To assess the accuracy of the method M06-2X/cc-pVTZ we calculated the relative energies of the tautomers **VII** and **VIII**.



VII



VIII

Energy of heterocyclic benzoid tautomer **VII** is less than that of the tautomer **VIII** with an open cycle by 1.7 kcal mol^{-1} (according to the experimental evaluation, by 1.0 kcal mol^{-1} [3]).

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