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1,2,3-Oxadiazole Rings in the Aromatic Compounds: A Quantum-Chemical Investigation

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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Abstract—Quantum chemical method PBE0/cc-pVTZ in conjunction with the polarizable continuum model (PCM) was applied to the calculation of the equilibrium structural parameters of the benzene and naphthalene 1,2,3-oxadiazole derivatives, as well as relevant diazocarbonyl compounds both in the free state and dissolved in dichloromethane. The calculated ionization potentials of benzo-1,2,3-oxadiazole (9.49 eV), 6-diazocyclohexa-2,4-dien-1-one (8.16 eV) and (6-oxocyclohexa-2,4-dien-1-ylidene)carbonyl (8.34 eV) differ from the experimental values no more than by 0.09 eV. The calculations indicate the possible existence of naphtho [2,3-*d*:6,7-*d*']bis(1,2,3-oxadiazole) in the gas phase and in aprotic solvents.

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1,2,3-Oxadiazole, in contrast to other oxadiazoles, is unstable and isomerizes into formyldiazomethane [1, 2]. However, according to the data of [3, 4] confirmed by quantum-chemical study [5], 1,2,3-oxadiazole ring is stabilized when condensed with a benzene ring, and in the gas phase benzo-1,2,3-oxa-diazole (**I**) is more stable than 6-diazocyclohexa-2,4-dien-1-one (**II**).

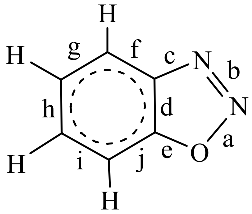
Using the quantum-chemical method (U)PBE0/cc-pVTZ with the GAUSSIAN-03 software [6], we calculated the ionization potentials of molecules **I**, **II**, and (6-oxocyclohexa-2,4-dien-1-ylidene)carbonyl (**III**). The closeness of the calculated *vertical* ionization potentials to experimental values (Table 1) obtained by photoelectron spectroscopy indicates the reliability of the proposed in [3] interpretation of the photoelectron spectra as those of the mixture of heterocyclic and diazocarbonyl tautomers.

Removing an electron from the benzo-1,2,3-oxadiazole molecule results in the heterocycle opening. Equilibrium structures of the radical cations $\mathbf{I}^+$ and $\mathbf{II}^+$ are identical. Therefore, the calculated *adiabatic* ionization potential 1.2 eV of the molecule **I** is less than the *vertical* ionization potential, while for molecules **II** and **III** the effects of nuclear relaxation do not exceed 0.2 eV. The opening of the heterocycle occurs also at the protonation of benzo-1,2,3-oxadiazole in acids due to the formation of aromatic cations $\mathbf{II}{\cdot}H^+$.

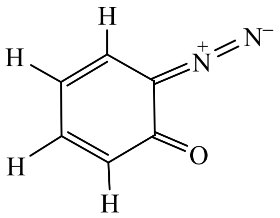
In this study, along with the polar molecules **I** (3.74 D) and **II** (4.08 D), we also investigated naphthalene derivatives **IV–VI**. Each structural formula is associated with a certain equilibrium configuration of atomic nuclei and a vibration spectrum, which contains no imaginary frequencies. Equilibrium configurations are characterized by the C_{2h} (**IV** and **VI**) or C_s (**V**) symmetry. The symmetry plane is the *xy* plane.

In contrast to the **I**↔**II** tautomeric transformation, the opening of heterocycles in the aromatic compound **IV** is not accompanied by the localization of double bonds in the naphthalene frame, as show the equilibrium length of the chemical bonds (Table 2). The lengths of the relatively short carbon–carbon bonds *g* and *i* decreased by 0.026 and 0.028 Å, respectively, at the opening of the heterocycle **I**, while the opening of heterocycle **IV** leads to some elongation of the short *f* and *j* bonds, by 0.021 and 0.053 Å, respectively. Unexpectedly, the long *d* bond in the free bis-zwitterion **VI** exceeds by length the corresponding bond in the molecule of **IV**, indicating a significant weakening in the former molecule of the conjugation effect of carbonyl with diazo group characteristic of α-diazocarbonyl compounds.

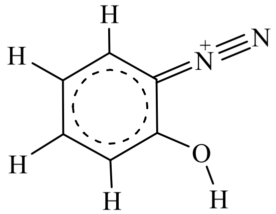
The effects of the interaction of molecules with the solvent we estimated based on the polarizable continuum model (PCM PBE0/cc-pVTZ). For determining the boundaries of the cavity occupied by a molecule or



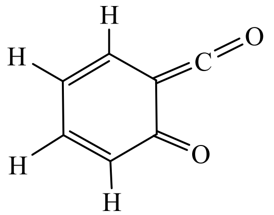
I



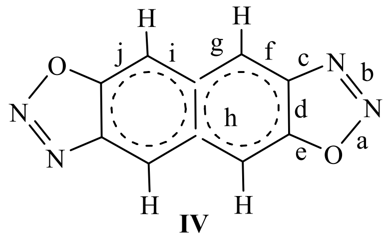
II



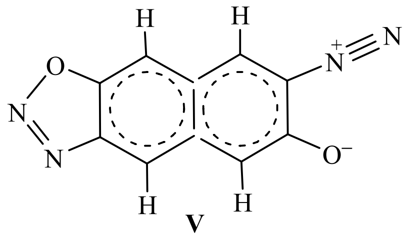
II•H$^+$



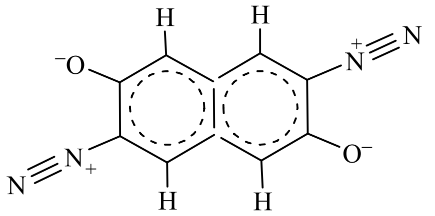
III



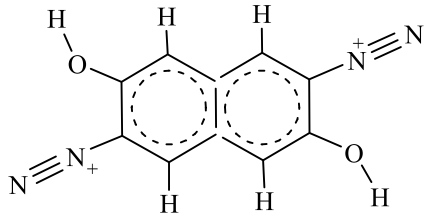
IV



V



VI



VI•2H$^+$

molecular ion in the solution we used the common values of the elementary sphere radius: C 1.925, CH 2.125, O 1.75 and N 1.83 Å.

According to the results of calculation, bis-heterocyclic isomer **IV** has a significant energy advantage over bis-zwitterionic isomer **VI** both in the free state (26 kcal mol^{-1} in vacuum) and in the polarizable aprotic medium (17 kcal mol^{-1} in dichloromethane). The opening of one of the two heterocyclic rings of molecule **IV** increases the energy by 11 kcal mol^{-1} in a vacuum and 7 kcal mol^{-1} in dichloromethane.

Table 1. Ionization potentials of molecules **I–III**, eV

Molecule	(U)PBE0[a]	Experiment [3]
Vertical ionization potential		
I	9.49	9.45[b]
II	8.16	8.20[b]
III	8.34	8.43[b]; 8.26[c]
Adiabatic ionization potential		
I	8.29 (8.20)	–
II	8.02 (8.00)	–
III	8.17 (8.16)	–

[a] Numbers in parentheses are obtained taking into account the zero point vibrations. [b] The method of photoelectron spectroscopy. [c] The mass spectrometric method.

The interaction of polar molecules **IV** and **VI** with the solvent does not lead to their dipole polarization, but affects significantly their quadrupole moments [7]. The opening of the two heterocycles in molecule **IV**, that is, its conversion into the bis-zwitterionic 2,6-bis(diazonio)naphth-3,7-oxide **VI**, is accompanied by an increase in magnitude of the two components of quadrupole moment, corresponding to the principal axes *x* and *y,* and a decrease in the transverse component corresponding to the main axis *z* orthogonal to the plane of the molecule (Table 3). The quadrupole moment of polar molecule **V** (dipole moment 3.74 D in a vacuum, 5.99 D in dichloromethane) is not discussed because it is not invariant toward the coordinate system (translation).

Despite some convergence of the energies of isomers **IV**–**VI** in a polarizable medium, bis-heterocyclic isomer **IV** retains the energy advantage over zwitterionic isomers **V** and **VI**. We should therefore expect that the molecules of naphtho[2,3-*d*:6,7-*d'*]bis(1,2,3-oxadiazole) containing two 1,2,3-oxadiazole rings are stable not only in the gas phase but also in polarized media free of labile protons, whose addition to the heterocycles would give the bis-diazonium dication **VI**·2H$^+$.

Table 2. The equilibrium bond lengths in molecules **I, II, IV–VI,** Å

Bond	**I**	**II**	$\mathbf{II}\cdot\mathrm{H}^+$	**IV**	**V**[a]	**VI**
In a vacuum						
NO (a)	1.433	3.276	3.275	1.437	1.436; 3.196	3.111
NN (b)	1.238	1.115	1.102	1.233	1.231; 1.112	1.110
CN (c)	1.381	1.319	1.357	1.388	1.393; 1.329	1.335
CC (d)	1.388	1.479	1.413	1.404	1.415; 1.491	1.501
CO (e)	1.332	1.222	1.323	1.338	1.344; 1.225	1.228
CC (f)	1.390	1.420	1.406	1.366	1.356; 1.398	1.387
CC (g)	1.380	1.354	1.369	1.410	1.428; 1.380	1.398
CC (h)	1.404	1.427	1.401	1.451	1.461	1.461
CC (i)	1.383	1.355	1.382	1.415	1.427; 1.383	1.396
CC (j)	1.387	1.450	1.389	1.363	1.353; 1.428	1.416
OH	–	–	0.964	–	–	–
In dichloromethane						
NO (a)	1.423	3.288	3.281	1.425	1.421; 3.240	3.197
NN (b)	1.241	1.111	1.100	1.236	1.235; 1.106	1.105
CN (c)	1.379	1.325	1.356	1.387	1.392; 1.338	1.344
CC (d)	1.388	1.468	1.411	1.403	1.411; 1.479	1.484
CO (e)	1.336	1.234	1.323	1.343	1.349; 1.240	1.244
CC (f)	1.392	1.418	1.404	1.367	1.360; 1.392	1.386
CC (g)	1.380	1.357	1.369	1.410	1.424; 1.385	1.399
CC (h)	1.406	1.424	1.401	1.452	1.456	1.454
CC (i)	1.383	1.360	1.381	1.415	1.424; 1.390	1.401
CC (j)	1.387	1.442	1.389	1.362	1.355; 1.418	1.409
OH	–	–	0.965	–	–	–

[a] The left numbers characterize the oxadiazole fragment, the right relate to the diazocarbonyl fragment of the molecule **V**.

Table 3. Principal values of the quadrupole moment of the molecule **IV** and bis-zwitterion **VI**, D, Å

Axis	**IV**	**VI**
In a vacuum		
x	–70.05	–98.76
y	46.49	87.07
z	23.56	11.69
In dichloromethane		
x	–90.71	–133.62
y	60.50	120.58
z	30.21	13.04

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