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Quantum-Chemical Study of Tautomers of Reduced Forms of Anthraquinone

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Abstract—The quantum-chemical method B3LYP/6-311G(d,p) was used to calculate structural parameters of four conformers of 9,10-dihydroxyanthracene, two conformers of 9-hydroxyanthrone, and the corresponding anions, dianion, and radical anion. The energy of 9,10-dihydroxyanthracene in a gas phase is higher and in aqueous solution lower than the energy of 9-hydroxyanthrone. The dianion can exist exclusively in a polarizable medium.

Keywords: 9,10-dihydroxyanthracene, hydroxyanthrone, tautomerism, structure, conformers, anions, quantum-chemical calculations

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The ability of anthraquinone to transfer electrons and catalyze redox reactions in condensed media [1–5] explains the interest in the structure and physicochemical properties of its reduced forms. The addition of an electron pair to anthraquinone converts it to either 9,10-dihydroxyanthracene (**I**) or 9-hydroxy-10-oxo-9,10-dihydroanthracene [9-hydroxyanthrone (**II**)]. The protolytic dissociation of these products in a polar solvent can give an anion, a dianion, and a radical anion.

In the present work we determined the equilibrium structural parameters and relative energies of the tautomers of hydrogenated anthraquinone tautomers and anionic forms of reduced anthraquinone in a gas phase and in a polarizable (aqueous) medium.

The quantum-chemical calculations were performed by the DFT B3LYP/6-311G(d,p) method using GAUSSIAN-03 [6]. Solvent effects were considered in the framework of polarizable continuum model (C-PCM) [7, 8]. The determination of equilibrium structural parameters of each molecule and ion was associated with vibrational analysis.

Varying the structural parameters of a free 9,10-dihydroxyanthracene molecule gave four energy minima corresponding to conformers **Ia**–**Id** with the symmetries C_2 (**Ia, Ic**), S_2 (**Ib**), and C_s (**Id**). Two protons in these conformers are forced out of the molecular plane by rotation of hydroxy groups around the C–O bond (Table 1, $C^{11}C^9OH$ or $C^{13}C^9OH$ dihedral angles). The deepest energy minimum corresponds to conformer **Ia**, but taking into account zero point correction makes the energy levels of conformers **Ia** and **Ib** to be quite close to each other, and those of conformers **Ic** and **Id** are placed higher by 0.3 kcal/mol. Due to the non-planarity, molecules **Ia, Ic,** and **Id** possess dipole moments (0.92, 2.23, and 2.44 D, respectively). Taking into account of the close energy of the tautomers and the negligibly low energy barriers to tautomeric transitions (<1 kcal/mol), for the dipole moment of 9,10-dihyd-roxyanthracene we can take as dipole moment value the highest of the above values (Scheme 1).

The calculated vertical and adiabatic ionization potentials of the tautomers of 9,10-dihydroxyanthracene in a vacuum are I^v 6.59–6.63 eV and I^a 6.45 eV. Polarization effects in aqueous solution decrease the calculated I^a values by 1.8 eV. Hydration of the emitted electron further decreases the ionization potentials by the difference in the electron work functions in a vacuum and in water.[1] Ionization increases the symmetry of equilibrium configurations to C_{2h} or C_{2v}. The radical cations possess planar structures.

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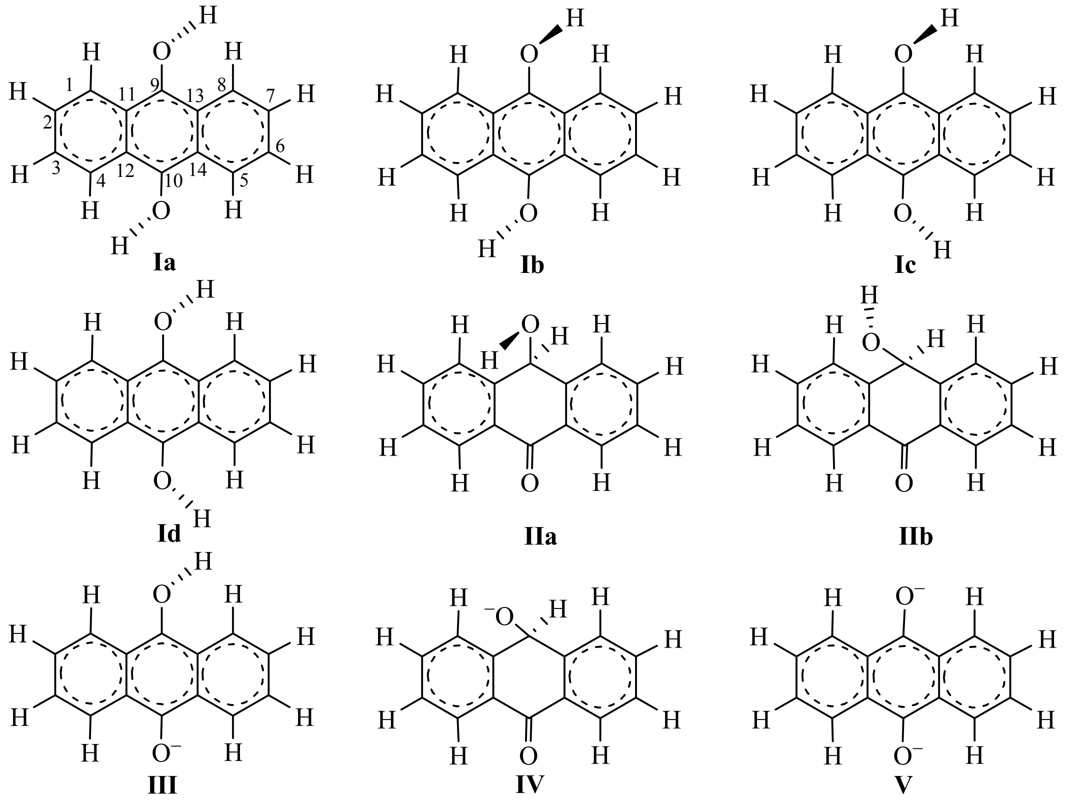
[1] Calculated ionization potential should be differentiated from the experimental ionization threshold of a molecule in solution.

Scheme 1.



The central rings in conformers **IIa** and **IIb** contain a four-coordinate carbon atom, and the phenylene fragments are not coplanar. Due to repulsion of the lone electron pairs of the hydroxyl oxygen from the π-electron system and incorporation of the proton into the latter [9], the energy of conformer **IIb** becomes higher than the energy of conformer **IIa** by 3 kcal/mol.[2] The dipole moment of the energetically favorable conformer **IIa** with an electrostatically favorable transoid arrangement of mobile protons (2.26 D) is lower compared with the dipole moment of *gauche* conformer **IIb** (3.55 D).

The calculations predict different relative energies of 9,10-dihydroxyanthracene and 9-hydroxyanthrone in a vacuum [E(**Ia**) > E(**IIa**) by 3 kcal/mol] and in solution [E(**Ia**) < E(**IIa**) by 3 kcal/mol]. According to [11, 12], the prevailing form of molecule **I** in alcohol solutions is that whose fraction in the equilibrium tautomer mixture is 89%.

Both the vertical (8.72 eV) and adiabatic (8.54 eV) ionization potentials of conformer **IIa** which prevails in a vacuum are 2.1 eV higher compared to the ionization potentials of conformers **Ia–Id**. The same difference in the ionization potentials of the tautomers (2.1 eV) is ramained in aqueous solution. The adiabatic ionization potentials of compounds **Ia** and **IIa** in water are 4.67 and 6.75 eV, respectively.

According to the calculations, the protolytic dissociation of both tautomers **I** and **II** gives 9,10-dihydroxyanthracene monoanion **III**. The concentration of anion **IV** formed by OH proton cleavage from 9-hydroxyanthrone is negligibly low, because the energy level of this tautomer by 23 kcal/mol in a vacuum and by 21 kcal/mol in water is higher compared that of monoanion **III**. The structural feature of the nonplanar monoanion **IV** is an equatorial position of the C^9–O^- bond and an axial position of the C^9–H bond, and, therewith, the equilibrium length of the latter bond (1.152 Å in a gas phase and 1.138 Å in solution) is greater a normal bond length in molecule **IIa**: 1.098 Å in a gas phase and 1.097 Å in solution.

The C–O^- bond length (1.25–1.27 Å) in monoanion **II** is closer to the C=O double bond lengths (1.22–1.23 Å) in 9-hydroxyanthrone (**II**) than to the C–OH single bond lengths (1.37–1.43 Å) in the monoanion

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[2] The energy gaps between conformers **IIa** and **IIb** were estimated by the modified interatomic potential method and by NMR at 5 kcal/mol [9] and 4 kcal/mol [10], respectively.

Table 1. (RO)B3LYP equilibrium structural parameters of 9,10-dihydroxyanthracene (**Ia**), 9-hydroxyanthrone (**IIa**), anions **III** and **V**, and radical anion **VI**

Parameter	Gas phase				Aqueous solution				
	Ia	**IIa**	**III**	**VI**	**Ia**	**IIa**	**III**	**V**	**VI**
Internuclear distance, Å									
C^1–C^2	1.367	1.390	1.374	1.379	1.369	1.391	1.373	1.374	1.380
C^1–C^{11}	1.427	1.398	1.430	1.412	1.429	1.398	1.432	1.425	1.414
C^2–C^3	1.421	1.397	1.415	1.413	1.423	1.398	1.419	1.425	1.412
C^3–C^4	1.368	1.386	1.380	1.379	1.369	1.387	1.377	1.374	1.380
C^4–C^{12}	1.429	1.402	1.408	1.412	1.429	1.404	1.416	1.425	1.414
C^9–C^{11}	1.403	1.518	1.404	1.465	1.406	1.518	1.406	1.441	1.462
C^{10}–C^{12}	1.405	1.490	1.466	1.465	1.407	1.486	1.455	1.441	1.462
C^{11}–C^{12}	1.442	1.403	1.440	1.425	1.444	1.404	1.443	1.453	1.426
C^{10}=O	–	1.220	–	–	–	1.227	–	–	–
C–O^-	–	–	1.251	1.254	–	–	1.269	1.298	1.261
C^9–OH	1.372	1.428	1.413	–	1.372	1.428	1.401	–	–
O–H	0.962	0.965	0.964	–	0.979	0.966	0.979	–	–
C^1–H	1.082	1.083	1.088	1.084	1.084	1.085	1.088	1.087	1.085
C^2–H	1.084	1.084	1.086	1.086	1.087	1.087	1.087	1.088	1.087
Bond and dihedral angles, deg									
$C^{11}C^9C^{13}$	121.0	114.2	121.1	115.8	120.7	114.2	120.6	114.9	116.4
$C^{12}C^{10}C^{14}$	121.0	117.0	115.4	115.8	120.7	117.4	115.9	114.9	116.4
C^9OH	109.3	107.4	107.3	–	111.3	107.8	108.8	–	–
$C^{11}C^9$OH	–158.4	65.1	–95.4	–	–141.7	65.2	–75.4	–	–
$C^{13}C^9$OH	22.7	–65.1	85.4	–	41.4	65.2	107.0	–	–

III and molecules **I** and **II**. The C–O^- bonds in dianion **V** are shorter than the C–OH bonds in dihydroxyanthracene **I** and hydroxyanthron **II** but longer than the C–O^- bond in 9,10-dihydroxyanthracene monoanion **III**.

The negative adiabatic ionization potential (−1.8 eV), calculated by the (U)B3LYP and (RO)B3LYP methods, points to the instability of dianion **V** in a gas phase.[3] However, inclusion of the interaction of the dianion with the polarizable aqueous medium increases the ionization potential to 2.47 eV [(U)B3LYP] or 2.50 eV [(RO)B3LYP]. The calculations predict a 4-fold decrease of the difference in the ionization potentials of the dianion and electrically neutral 9,10-dihydroxyanthracene molecules from 4.86 eV in a vacuum and 1.25 eV in water.

Electron capture by the anthraquinone molecule and electron cleavage from dianion **V** give rise to radical anion **VI**. We can suggest two alternative structural formulas **VIa** and **VIb** for this anion, which

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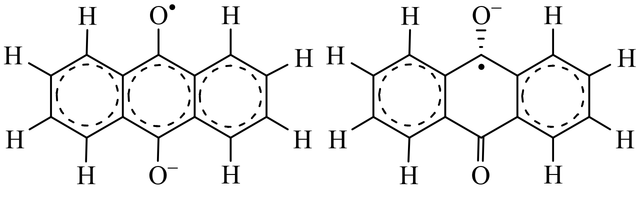
[3] After inclusion in the basis set of diffuse functions of carbon and oxygen the dianion ionization potential remains negative and its module even increases: I^v 2.44 eV, I^a 2.50 eV.

Table 2. (RO)B3LYP atomic charges and free valences in radical anion **VI**

Gas phase					Aqueous solution				
O	C^1	C^2	C^9	C^{11}	O	C^1	C^2	C^9	C^{11}
Atomic charges (NPA [14, 15]), a.u.									
–0.678	–0.172	–0.230	0.437	–0.116	–0.730	–0.184	–0.219	0.435	–0.128
Free valences, a.u.									
0.172	0.011	0.034	0.109	0.064	0.164	0.016	0.033	0.122	0.058

correspond to the symmetry groups C_{2v} and C_s. Structure **VIa** is formed by proton cleavage from the hydroxyl hydrogen in monoanion **III**, and structure **VIb,** by proton cleavage from the four-coordinate carbon atom in monoanion **IV** (Scheme 2). Restricted and unrestricted B3LYP calculations confirm neither of these structures but suggest a high symmetry (D_{2h}) of radical anion **VI**. The electron charge is equally distributed between oxygen atoms. The free valence is mostly distributed between oxygens and neighboring carbon atoms (Table 2).[4] The (RO)B3LYP adiabatic ionization potential of the radical anion is positive: 1.59 eV in a vacuum and 3.42 eV in water.

Scheme 2.



VIa **VIb**

Thus, our calculations point to nonplanarity and polarity of 9,10-dihydroxyanthracene. The structural parameters of the four energetically close conformers and anionic and dianionic forms of reduced anthraquinone differ from those suggested previously in a comparative study of the electron-donor ability and reactivity of anthraquinone and model compounds containing a lignin structural unit in the presence of reducing agents in aqueous alkali [2].

The effect of a polarizable medium (water) is so strong that the electron-donor properties and tautomer ratio in reduced anthraquinone forms are impossible to estimate neither quantitatively nor qualitatively without taking this effect into consideration. In particular, the difference in the ionization potentials of 9,10-dihydroxyanthracene and its dianion in water decreases 4-fold. According to the calculations, the dianion can exist exclusively in solution.

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[4] The free valence of an atom (A) is characterized by the index D_A proposed in [13].

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