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p-Hydroxyphenyldiazonium Cation and Conjugated Base: A Quantum Chemical Study

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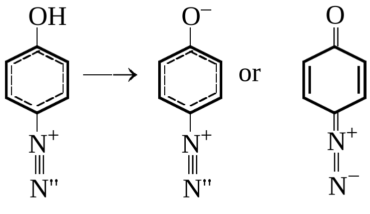
Abstract—Structural parameters and IR spectra of *p*-hydroxyphenyldiazonium cation and its conjugated base and of their monohydrates in the free state and in aqueous solution were calculated by the B3LYP/6-311G** method. The effects of aqueous medium were taken into account using the polarizable continuum model (PCM). The conjugated base is not a quasiaromatic *p*-diazoniophenolate zwitterion but has an essentially quinoid structure of 4-diazocyclohexa-2,5-dien-1-one. Its dipole moment in water (8 D) is much lower than that of *p*-diazoniobenzenesulfonate zwitterion (24 D).

p-Hydroxyphenyldiazonium salts, when dissolved in water, form cations $[NNC_6H_4OH]^+$ (**I**), which can be considered as aromatic benzene derivatives. Owing to simultaneous presence of a proton-donating hydroxy group and an electronegative diazonium group, cation **I** has so strong acidity that it does not form diazotates under the action of alkaline reagents [1, 2]. In aqueous solutions of various acidities, the *p*-hydroxyphenyldiazonium cations are in equilibrium with their conjugated bases (**II**). Therefore, it is not always clear what form enters into a specific chemical reaction [1]. In some cases, both molecular forms can react simultaneously. In a weakly acidic (due to partial hydrolysis) aqueous medium containing zinc and cobalt chlorides, crystalline complexes $[(HOC_6H_4NN)_2(OC_6H_4NN)]^{2+}[MtCl_4]^{2-}$ are formed, whereas mercury(II) chloride forms an adduct with the base, $\mathbf{II} \cdot HgCl_2$ [3], and azo coupling occurs with the diazonium form exclusively [1]. Protolytic dissociation of cation **I** should yield either diazoniophenolate with zwitterionic benzoid structure **IIA** [2] or 4-diazocyclohexa-2,5-dien-1-one of *p*-quinoid structure **IIB**.



I **IIA** **IIB**

In this study we calculated the equilibrium configurations, IR spectra, atomic charges, and dipole moments of **I**, **II**, $\mathbf{I} \cdot OH_2$, and $\mathbf{II} \cdot HOH$, and also those of *p*-benzoquinone (BQ), phenol (PhOH), complex $PhOH \cdot OH_2$, and *p*-diazoniobenzenesulfonate **III** by DFT B3LYP/6-311G(d_5,p) method using the GAUSSIAN package [4]. For the hypervalent sulfur atom, the basis set was extended to 6-311G($3d_5f_7$). The nonspecific influence of the aqueous medium (aq) on the molecules, molecular ions, and complexes was estimated within the framework of the polarizable continuum model (PCM).

On substitution of the diazonium group for hydrogen in the *para* position of phenol, the C–O interatomic distance decreases by 0.04 Å, the two C–C bonds "parallel" to NNC–CO axis become shorter, and the other four bonds of the ring become longer. The structure of the cation appears to be intermediate between the benzoid phenolic and quinoid *p*-benzoquinone structures. The quinoid character of the ring becomes more pronounced when the hydrogen bonding of the hydroxy group with the water molecule is taken into account and slightly less pronounced when the aqueous medium is simulated by a dielectric continuum (Fig. 1).

The polarizable medium enhances the hydrogen bonding in phenol and *p*-hydroxyphenyldiazonium monohydrates. In $PhOH \cdot OH_2$, the O···O interatomic distance, which in the free state is equal to the sum of the van der Waals radii, decreases by 0.100 Å on transferring the complex into water. In the *p*-hydroxyphenyldiazonium cation monohydrate, the equilibrium O···O internuclear distance is 0.047 Å shorter in the aqueous medium compared to the free molecule. At the same time, the effects of hydrogen bonding and polarization of the medium do not appreciably affect the NN bond length in the cation.

Strengthening of the hydrogen bond in all the

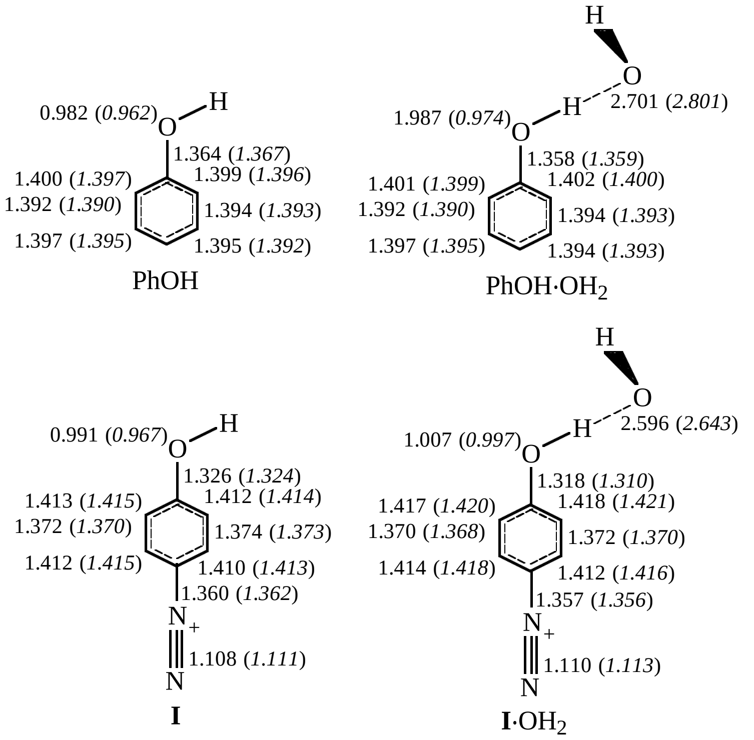


Fig. 1. Calculated interatomic distances (Å) in phenol (PhOH), its monohydrate (PhOH · OH_2), *p*-hydroxyphenyldiazonium (**I**), and its monohydrate (**I** · OH_2) in water and in the free state (in parentheses, italic).

above cases is accompanied by an increase in the O–H interatomic distance, which attains 1.007 Å in the hydrate **I** · OH_2/aq. In other words, the H-bond becomes more symmetrical on shortening. The effect of the polarizable medium on the cationic complex **I** · OH_2/aq (but not on PhOH · OH_2/aq) appears as an increase by 0.008 Å of the C–O interatomic distance, which is 0.017–0.025 Å longer than the average bond length (1.293 Å) in the phenol and *p*-benzoquinone molecules.

The conjugated base of *p*-hydroxyphenyldiazonium cation, as judged from the equilibrium interatomic distances (Fig. 2), has essentially quinoid structure of 4-diazocyclohexa-2,5-dien-1-one (**IIB**). Even such a highly polar solvent as water is incapable to stabilize the alternative zwitterionic benzoid structure **IIA**, which could be expected to be prevalent at least owing to its aromaticity. Such a structure is indeed found for **III** (Fig. 3).

The equilibrium Cartesian coordinates of the atomic nuclei, calculated for monohydrates **I** · OH_2/aq and **II** · HOH/aq and for zwitterion **III**/aq, are listed in Table 1.

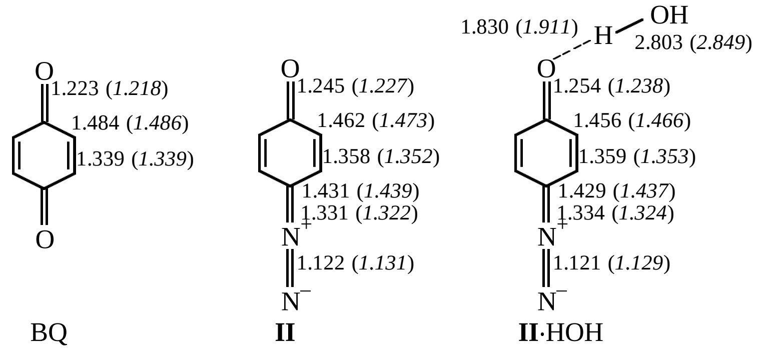


Fig. 2. Calculated interatomic distances (Å) in *p*-benzoquinone (BQ), 4-diazocyclohexa-2,5-dien-1-one (**II**), and its monohydrate (**II** · HOH) in water and in the free state (in parentheses, italic).

Table 1. Cartesian coordinates of atomic nuclei in complexes **I** · OH_2/aq and **II** · HOH/aq and in zwitterion **III**/aq, Å

Atom	**I** · OH_2/aq			**II** · HOH/aq			**III**/aq		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
C	1.056	0.553	0.000	1.110	0.687	–0.025	–0.421	0.016	0.003
C	0.616	–0.795	0.000	0.722	–0.717	–0.053	0.271	1.231	–0.003
C	–0.726	–1.083	0.000	–0.580	–1.104	–0.041	1.656	1.243	–0.004
C	–1.642	–0.009	0.000	–1.600	–0.104	0.002	2.307	0.002	–0.000
C	–1.231	1.344	0.000	–1.278	1.287	0.033	1.642	–1.236	0.007
C	0.113	1.611	0.000	0.030	1.660	0.020	0.261	–1.209	0.009
H	1.347	–1.596	0.000	1.520	–1.450	–0.088	–0.278	2.166	–0.005
H	–1.087	–2.109	0.000	–0.866	–2.153	–0.064	2.227	2.169	–0.009
H	–1.973	2.140	0.000	–2.082	2.018	0.066	2.205	–2.167	0.010
H	0.476	2.635	0.000	0.305	2.711	0.043	–0.292	–2.145	0.015
N	–2.971	–0.286	0.000	–2.881	–0.478	0.012	3.685	–0.005	–0.003
N	–4.058	–0.510	0.000	–3.956	–0.792	0.019	4.788	–0.010	–0.005
O/S	2.333	0.881	0.000	2.312	1.046	–0.041	–2.230	–0.001	–0.002
H	2.937	0.076	0.000	–	–	–	–	–	–
O/O	3.850	–1.226	0.000	4.059	1.146	–0.037	–2.630	1.400	0.017
H/O	4.436	–1.308	–0.776	3.512	–0.336	–0.071	–2.584	–0.737	1.206
H/O	4.436	–1.308	0.776	4.076	–1.361	0.909	–2.574	–0.699	–1.235

All the normal modes of the compounds in question are characterized by real wave numbers ν. Hence, each calculated equilibrium nuclear configuration corresponds to an energy minimum. Some of vibrations are characterized by high IR intensities. In particular, the vibration bands of the diazo group in **I**, **I** · OH_2, **II**, and **II** · HOH, of the carbonyl group in **II** and **II** · HOH, and of hydrogen-bonded hydroxy group in **I** · OH_2 are very strong (Table 2).

Hydrogen bonding decreases the wave number of the IR band corresponding to diazo group in the *p*-hydroxyphenyldiazonium cation and increases ν(NN) in the conjugated base; as a result, the difference between these two wave numbers, Δν(NN), decreases from 110 to 86 cm^{-1}. The calculated intensity of this band is higher in the case of hydrogen bonding.

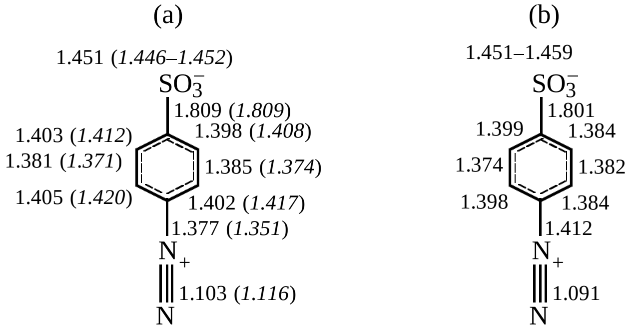


Fig. 3. Interatomic distances (Å) in *p*-diazoniobenzenesulfonate (**III**): (a) calculated values in water and in the free state (parentheses, italic) and (b) experimental data (single crystal X-ray diffraction [5]).

The aqueous medium as a dielectric continuum increases both the intensity of all the IR bands considered and the wave numbers ν(NN) for **I**, **II**, **I** · OH_2, and **II** · HOH, but decreases ν(C=O) and ν(OH). The aqueous medium affects the wave number ν(NN) in the IR spectrum of zwitterion **III** much more strongly than in the spectra of **I**/aq and **II**/aq. The intensity of out-of-plane vibration ($\perp$) of the hydrogen-bonded H atom indicates that its effective charge increases when the cationic complex **I** · OH_2 is immersed in a polarizable continuum.

As follows from review [1], the experimental spectra of base **II** published by various authors include a ν(NN) band with maxima at 2088, 2109, and 2110 cm^{-1}. Our calculated ν(NN) values (Table 2) are slightly higher, but the wave number ν(C=O) calculated for **II** · HOH/aq is exactly the same as the experimental value of 1578 cm^{-1} [1].

We calculated the atomic charges by differentiating the dipole moment of a molecule or molecular ion with respect to z_A coordinates of atomic nuclei (*A*) along the normal to the symmetry plane (*xy*) in which these nuclei are arranged in their equilibrium positions [6]. Such charges $q^{\perp}$, unlike the q^{APT} charges sug-

Table 2. Calculated IR wave numbers (ν) and band intensities (A)

Localization of normal mode	Compound	ν, cm^{-1}		A, km mol^{-1}	
		free state	aqueous solution	free state	aqueous solution
NN"	**I**	2308	2325	469	1109
	I·OH_2	2293	2313	609	1313
	II	2199	2215	1086	2506
	II·HOH	2207	2227	1092	2377
	III	2269	2367	1144	735
C=O	BQ	1742	1700	378[a]	546[a]
	II	1701	1601	513	557
	II·HOH	1669	1578	654	954
OH	PhOH·OH_2	3614	3351	729	1700
	I·OH_2	3205	2967	–[b]	3565
H (⊥)	PhOH·OH_2	793	886	66	139
	I·OH_2	1044	1061	104	137

[a] A half of A for antisymmetric vibration. [b] Intensity was not determined because of the resonance of the OH and CH vibrations.

gested in [7], allow the dipole moment of a planar molecule (or molecular cation) to be reproduced in accordance with the precise formula

$$\mu = \Sigma_A Z_A r_A - \int r\rho(r)dv = \Sigma_A q_A^{\perp} r_A,$$

where $\mu_z = 0$, Z_A is the charge of atomic nucleus, r_A is its radius-vector, and $\rho(r)$ is the electron density in the atomic system.

The sum of atomic charges coincides with the charge of the free molecule (or molecular ion). However, in a polarizable medium, the sum of all $q_A^{\perp}$ (as well as the sum of all q_A^{APT}) in the PCM approximation is overestimated and has a value of +1.21 instead of +1 au for cation **I**/aq and +0.10 instead of 0 au for molecule **II**/aq. Nevertheless, we suggest that, for planar or approximately planar molecules, the $q_A^{\perp}$ charges are preferable over the alternative q_A^{APT}, q_A^M, q_A^{NPA}, q_A^E, and q_A^B values. The method for calculating the Mulliken charges q_A^M [8], based on the orbital representation of atoms, becomes incorrect in going from the minimum AO basis to extended sets of Gauss functions (see, e.g., [9]). In the “natural” population analysis [10], the averaging of the diagonal blocks of the electronic population matix and, especially, similar averaging of the overlap integrals, preceding the evaluation of the natural populations and orbitals, seem doubtful. The population analysis of “polarized extract-orbitals” localized in the vicinity of atomic nuclei [11] gives the charges q_A^E that depend too strongly on both the choice of the localization criterion and the intuitively chosen k_A parameters arbitrarily included in the corresponding functional (see Table 1 in [11]). The Bader’s procedure [12] can lead to charges q_A^B that are improbable from the chemical viewpoint. For example, for the hypervalent nitrogen atoms N^+ in the zwitterions $H_2C{=}N^+{=}N^-$ and $H_3C{-}C{\equiv}N^+{-}O^-$, the calculated charges are –0.83 (H_2CNN), –0.84 (H_2CNN/aq), –0.90 (MeCNO), and –0.98 (MeCNO/aq) [13].

Regardless of the calculation method, the atomic charges reflect strong effect of the medium on the electronic structure of the molecules and cations considered (Table 3). The charge of diazo group $q_{NN''}^{\perp} = q_N^{\perp} + q_{N''}^{\perp}$ in the solvate **II**·HOH/aq is lower than that in the cationic complex **I**·HOH/aq and zwitterion **III**/aq (0.28, 0.42, and 0.48 au, respectively). The charges $q_{N''}^{\perp}$ of the terminal nitrogen atoms are insignificant. They are positive in **I** and negative in **II**. The charge of the oxygen atom **II** is comparable with that of oxygen in **I** and cationic complex **I**·OH_2, which is inconsistent with the zwitterionic structure **IIA**. The charge transfer to the water molecule in the free cationic complex **I**·OH_2 is 1.5 times greater than in the electrically neutral complex PhOH·OH_2. An increase in charge transfer is accompanied by strengthening of hydrogen bonding.

The calculated dipole moment of 4.5 D of free molecule **II** reasonably agrees with the experimental estimate of 5.0 D [1]. With $q_A^{\perp}$ atomic charges, it can be considered as a precise sum of the dipole moments of the chemical bonds (but not atomic groups bearing electric charge) [14]. In so doing, the C=O bond polarity is characterized by a dipole moment of 2.254 (for **II**) or 2.257 D (for **II**·HOH).

Table 3. Atomic charges $q^{\perp}$, q^{NPA}, and q^{M}, au

Atom or group	Compound	Free state			Aqueous solution		
		$q^{\perp}$	q^{NPA}	q^{M}	$q^{\perp}$	q^{NPA}	q^{M}
N	**I**	0.280	0.131	0.018	0.404	0.166	0.054
	I · OH_2	0.271	0.127	0.010	0.396	0.162	0.048
	II	0.214	0.083	–0.044	0.340	0.124	0.006
	II · HOH	0.220	0.088	–0.039	0.350	0.130	0.011
	III	0.249	0.127	0.005	0.401	0.180	0.074
	H_2CNN	0.186	0.048	0.089	0.226	0.060	0.100
N"	**I**	0.059	0.263	0.107	0.034	0.239	0.085
	I · OH_2	0.041	0.237	0.086	0.024	0.226	0.075
	II	–0.090	0.062	–0.057	–0.076	0.103	–0.025
	II · HOH	–0.082	0.075	–0.047	–0.065	0.119	–0.012
	III	0.002	0.183	0.040	0.078	0.286	0.122
	H_2CNN	–0.131	–0.036	–0.133	–0.194	–0.084	–0.176
SO_3	**III**	–	–0.470	–0.706	–	–0.695	–0.960
O	PhOH	–0.373	–0.670	–0.362	–0.481	–0.708	–0.419
	PhOH · OH_2	–0.371	–0.700	–0.391	–0.467	–0.724	–0.429
	I	–0.317	–0.591	–0.270	–0.433	–0.643	–0.345
	I · OH_2	–0.307	–0.611	–0.299	–0.410	–0.649	–0.355
	II	–0.383	–0.569	–0.338	–0.551	–0.681	–0.460
	II · HOH	–0.379	–0.615	–0.389	–0.540	–0.702	–0.481
	BQ	–0.339	–0.494	–0.278	–0.448	–0.546	–0.342
H	PhOH	0.331	0.460	0.246	0.435	0.511	0.318
	PhOH · OH_2	0.279	0.487	0.249	0.346	0.498	0.274
	I	0.360	0.495	0.290	0.456	0.539	0.353
	I · OH_2	0.287	0.511	0.300	0.347	0.507	0.305
H_2O	PhOH · OH_2	0.105	0.031	0.077	–	0.053	0.106
	I · OH_2	0.161	0.061	0.110	–	0.079	0.131
	II · HOH	–	–0.017	–0.003	–	–0.032	–0.030

Molecule **II** is characterized by high longitudinal polarizability α_{xx} and hyperpolarizability β_{xxx}. Due to interaction of the molecule with aqueous medium, the dipolar polarizability α_{xx} grows by 61% ($24.3 \rightarrow 39.1$ Å^3), and the hyperpolarizability β_{xxx} grows sixfold ($431 \rightarrow 2534$ au). However, the dipole moment of molecule **II**/aq polarized by the reactive field (8.1 D) is much less than that of zwitterion **III**/aq (24.0 D).

Thus, our quantum chemical calculations show that the quinoid character of the six-membered ring in the *p*-hydroxyphenyldiazonium cation is more pronounced than that in phenol or PhOH · OH_2. The hydrogen bonding of the hydroxy group with the water molecule enhances this effect of the diazonium group. The polarizable medium enhances the hydrogen bonding in phenol and *p*-hydroxyphenyldiazonium monohydrates. The protolytic dissociation of the *p*-hydroxyphenyldiazonium cation in aqueous medium yields quinoid 4-diazocyclohexa-2,5-dien-1-one whose molecule is characterized by high values of the dipole moment, polarizability, and hyperpolarizability but, unlike the *p*-diazoniobenzenesulfonate molecule, is not an aromatic zwitterion.

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