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Tautomers of 4,5-Dihydroxy-1,8-bis(dimethylamino)naphthalene and Related Boron Compounds: A Quantum-Chemical Study

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Abstract—The quantum-chemical method PBE0/cc-pV(D,T)Z was applied to determine structural parameters, relative energies, and dipole moments of the prototropic tautomers of 4,5-dihydroxy-1,8-bis(dimethylamino) naphthalene. According to the calculations, this compound can exist in the gas phase as low-polar molecules with one asymmetric intramolecular hydrogen bond. In a polarizable medium a pair of zwitter-ionic tautomers dominate of similar energy with two asymmetric intramolecular hydrogen bonds. These tautomers and a hypothetic heterocyclic analog containing a BH_2^+ group instead of a proton between the nitrogen atoms are characterized by a high value of dipole moment and first hyperpolarizability. Mutual transformation of enantiomers (mirror antipodes) when transferring a proton from the hydroxy group to a neighboring atom in the O-boron-containing zwitter-ion is an example of strictly degenerate prototropic tautomerism.

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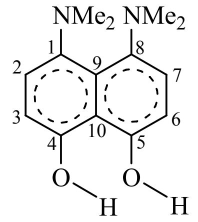
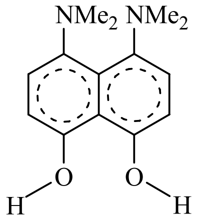
The problem of the synthesis and physicochemical study of 4,5-dihydroxy-1,8-bis(dimethylamino)naphthalene (**I**) arises from the assumption of its high basicity. In [1] at the synthesis of the hydrobromide **I**·HBr and processing it with an equivalent amount of lithium diisopropylamide in a binary solvent DMSO/cyclohexane instead of the expected compound **I** a zwitter-ionic tautomer **II** was obtained. According to XRD analysis of the reaction product, the molecules in the crystal possess the structure **II-e*** [1].[1]

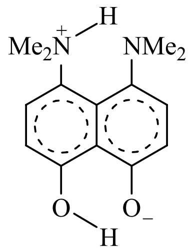
Nevertheless, the molecule **I**, among other derivatives of 1,8-bis(dimethylamino)naphthalene was discussed in [2]. Quantum-chemical calculations (B3LYP/6-31G** and B3LYP/6-311++G**), performed in this study confirm the high proton affinity of tautomer **I,** superior to that of 1,8-bis(dimethylamino)-naphthalene by almost 4 kcal mol^{-1}.



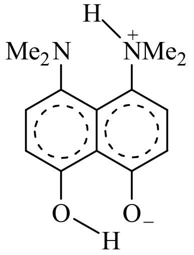
I



I-a



II-z



II-e

In this paper, by PBE0 method using the cc-pVTZ (for the atoms N, O, and related labile hydrogen atoms H) and cc-pVDZ orbitals (for C and H atoms of naphthalene and methyl fragments) with the Gaussian-03 software [3], we performed quantum-chemical calculations of the equilibrium structural parameters, IR spectra, dipole moments, and relative energies of tautomers **I**, **I-a**, **II-e**, and **II-z**. in gas phase and in acetonitrile solution.

To assess the effects of the polarizable medium we used the PCM model [4, 5]. In determining the boundaries of the cavity occupied by the molecule in solution we set the constant radii of the spheres for the following atoms and atomic groups: C 1.925, CH

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[1] The letters e and z used in marking the tautomers, as well as the stereochemistry descriptors *E, Z*, are derived from the words *entgegen* and *zusammen*. Numbering of atoms in the ions and zwitter-ions corresponds to the numbering of the atoms in the molecule **I**.

2.125, CH_3 2.525, N 1.83, O 1.75 Å, and labile H atom 1.443 Å. Relevance of the equilibrium internuclear distances (Table 1) to the energy minima was confirmed by the absence of imaginary frequencies in the vibrational spectra.

The calculations indicate a significant structural difference between molecules **I**, **I-a**, and **II**. Molecule **I** is unsymmetrical, and the equilibrium structure of **I-a** is characterized by C_2 symmetry. Both molecules include nonplanar naphthalene fragment. One of the carbon atoms (C') of each $N(CH_3)_2$ group is located near the average plane of the naphthalene moiety, while the second (C") is distant from this plane. In view of their structural features, each of the molecules **I** and **I-a** has a pair of equivalent (enantiomeric) equilibrium configurations in which the atoms C" are located on the opposite sides of the naphthalene fragment.

The space between the nuclei of nitrogen atoms is occupied by lone electron pairs. When a proton is introduced to one of two equivalent lone pairs of nitrogen atoms, the **I** → **II** conversion leads to a rotation of both $N(CH_3)_2$ groups around the C–N bond. As a result, the zwitter-ion acquires a symmetry plane, in which lie the nuclei of the atoms of naphthalene fragment, nitrogen and oxygen. Due to the asymmetry of the intermolecular hydrogen bonds a pair of prototropic tautomers **II-e** and **II-z** with C_s symmetry can exist.

The comparison of the calculated relative energies of the molecules (Table 2) leads to the conclusion that in the free state the low-polar tautomer **I** with an asymmetric intramolecular hydrogen bond $O^4–H\cdots O^5$ is preferable by energy. The structure of **I-a**, in which the labile hydrogen atom of the hydroxy group is the most distant from the neighboring atom O^5, corresonds to a local minimum of the molecular energy. Conformational transition **I** → **I-a** is accompanied by the rupture of hydrogen bonds and requires the expenditure of 7 kcal mol^{-1}. A significant contribution to this value obviously brings the repulsion of unshared electron pairs of oxygen atoms in the structure **I-a**.

Energy of two zwitter-ionic prototropic tautomers **II-z** and **II-e**, every one of them including two asymmetric hydrogen bonds (O–H···O and N–H···N), differ only by 0.1 kcal mol^{-1} (with accounting for the "zero" fluctuations). The calculation of the equilibrium structure of zwitter-ion within C_{2v} point symmetry group gave two imaginary wave numbers in the vibrational spectrum: i853 and i657 cm^{-1}, which corresponded to the antisymmetric and symmetric vibrations of the two labile protons. This structure corresponds to a potential barrier of the two-proton intramolecular transfer, that is, synchronous proton transfer within the O–H···O and $N^+–H\cdots N$ hydrogen bonds. The calculated barrier height is 1.4 kcal mol^{-1} relative to **II-e** and 0.7 kcal mol^{-1} relative to **II-z**. When taking into account the "zero" vibrations in the harmonic approximation, the energy barrier disappears.

The solvent reactive field increases the polarity of tautomers **II** and stabilizes them with respect to the transformation into tautomer **I**. Therefore, in acetonitrile and other polar solvents the zwitter-ions **II** dominate over the low-polar molecules **I**. It is presumable that the low-polar tautomers are present in the defects of the crystal lattice resulting from topochemical reaction of proton transfer from the nitrogen atoms of one molecule to the oxygen atoms of the neighboring molecule.

The pale yellow monoclinic crystals of the space group $P2_1/n$ characterized by the presence of four **II-e** molecules in the cell [1] cannot have the non-linear optical properties and generate the second harmonic of laser radiation due to their symmetry. However, under certain conditions, a solution of the zwitter-ion **II** oriented by the external electric field, showing no maximum in the visible light absorption (Table 3) and having high first hyperpolarizability (Table 4) can be used as a nonlinear optical medium. By the calculated molecular electro-optical characteristics, the zwitter-ionic tautomers **II-e** and **II-z** are superior to the *m*-nitroaniline [6] and vanillin [7,8] possessing nonlinear optical properties.

The equilibrium structures **II-e** and **II-z** are characterized by the C_s point group symmetry. Therefore, the absolutely symmetric tensor of first hyperpolarizability $\boldsymbol{\beta}$ contains no more than six different non-zero components (β_{xxx}, β_{yyy}, β_{xxy}, β_{xyy}, β_{xzz}, β_{yzz}) with the numerical values depending on the orientation of the coordinate axes. As the first hyperpolarizability invariants, we consider the norm $|\mathbf{b}|$ of vector **b**, which is obtained by convolution of the tensor $\boldsymbol{\beta}$ according to Eqs. (1a)–(1c) and the projection of this vector on the direction of the dipole moment μ, defined by formula (2):

$$b_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}, \tag{1a}$$

$$b_y = \beta_{yyy} + \beta_{yxx} + \beta_{yzz}, \tag{1b}$$

$$b_z = 0, \tag{1c}$$

$$b_\mu = \mathbf{b}\cdot\boldsymbol{\mu}/\mu. \tag{2}$$

Table 1. Equilibrium internuclear distances in the tautomers **I** and **II**, cations **II**·H$^+$, and boron-containing isomers **III** and **IV**, Å

Bond	**I**	**I-a**	**II-e**	**II-z**	(**II-e**)·H$^+$	(**II-z**)·H$^+$	**III**	**IV**
Gaseous phase								
C^1–C^2	1.386	1.383	1.386	1.384	1.381	1.377	1.384	1.385
C^1–C^9	1.442	1.446	1.427	1.425	1.424	1.424	1.423	1.417
C^2–C^3	1.399	1.401	1.393	1.392	1.393	1.393	1.392	1.407
C^3–C^4	1.377	1.376	1.398	1.403	1.386	1.387	1.397	1.384
C^4–C^{10}	1.433	1.431	1.430	1.433	1.434	1.436	1.431	1.428
C^5–C^{10}	1.426	1.431	1.458	1.453	1.428	1.427	1.455	1.424
C^5–C^6	1.369	1.376	1.421	1.416	1.377	1.376	1.418	1.377
C^6–C^7	1.404	1.401	1.384	1.387	1.401	1.401	1.383	1.413
C^7–C^8	1.383	1.383	1.390	1.392	1.373	1.375	1.394	1.373
C^8–C^9	1.449	1.446	1.423	1.422	1.430	1.432	1.419	1.420
C^9–C^{10}	1.445	1.446	1.430	1.429	1.441	1.441	1.432	1.428
C^1–N^1/C^1–B	1.414	1.412	1.461	1.471	1.456	1.469	1.478	1.583
C^8–N^8	1.409	1.412	1.471	1.461	1.468	1.455	1.480	1.442
C^4–O^4	1.355	1.361	1.321	1.314	1.337	1.335	1.318	1.355
C^5–O^5	1.381	1.361	1.275	1.282	1.360	1.362	1.277	1.375
N–Me'/N^1–Me	1.441	1.441	1.465	1.478	1.472	1.483	1.488, 1.491	1.442
N–Me"/N^8–Me	1.452	1.452	1.479	1.466	1.482	1.471	1.496, 1.491	1.460
N^1–H/N^1–B	–	–	1.543	1.123	1.467	1.110	1.593	1.425
N^8–H/N^8–B	–	–	1.105	1.505	1.137	1.522	1.595	2.144
O^4–H^4	0.966	0.960	1.045	1.073	0.967	0.968	1.053	0.965
O^5–H^4	1.724	–	1.430	1.370	1.750	1.736	1.409	1.807
O^5–H^5	0.959	0.960	–	–	0.961	0.961	–	0.959
Solution in acetonitrile								
C^1–C^2	1.387	1.385	1.383	1.379	1.379	1.375	1.381	1.384
C^1–C^9	1.446	1.447	1.430	1.427	1.428	1.425	1.425	1.416
C^2–C^3	1.402	1.402	1.399	1.399	1.398	1.397	1.397	1.412
C^3–C^4	1.376	1.377	1.390	1.393	1.383	1.384	1.390	1.385
C^4–C^{10}	1.434	1.434	1.431	1.432	1.433	1.434	1.431	1.427
C^5–C^{10}	1.429	1.432	1.453	1.449	1.428	1.427	1.450	1.426
C^5–C^6	1.371	1.376	1.408	1.405	1.376	1.376	1.405	1.379
C^6–C^7	1.405	1.402	1.394	1.396	1.402	1.402	1.392	1.415
C^7–C^8	1.386	1.385	1.383	1.386	1.372	1.376	1.386	1.373
C^8–C^9	1.449	1.448	1.425	1.426	1.429	1.432	1.422	1.414
C^9–C^{10}	1.445	1.449	1.434	1.433	1.441	1.440	1.436	1.422
C^1–N^1/C^1–B	1.410	1.410	1.455	1.470	1.453	1.468	1.476	1.593
C^8–N^8	1.408	1.410	1.470	1.456	1.467	1.452	1.477	1.451
C^4–O^4	1.362	1.360	1.337	1.332	1.348	1.346	1.332	1.359
C^5–O^5	1.374	1.365	1.297	1.303	1.359	1.361	1.298	1.369
N–Me'/N^1–Me	1.443	1.443	1.467	1.482	1.470	1.483	1.495, 1.494	1.442
N–Me"/N^8–Me	1.452	1.452	1.482	1.467	1.483	1.469	1.497, 1.494	1.471
N^1–H/N^1–B	–	–	1.557	1.109	1.510	1.105	1.593	1.447
N^8–H/N^8–B	–	–	1.097	1.531	1.112	1.526	1.592	1.929
O^4–H^4	0.972	0.976	1.049	1.067	0.970	0.971	1.058	0.968
O^5–H^4	1.685	–	1.415	1.377	1.714	1.706	1.391	1.805
O^5–H^5	0.979	0.962	–	–	0.962	0.962	–	0.961

Table 2. Dipole moments (μ) and relative energies (Δ*E*) of molecules

Molecule	μ, D		Δ*E*, kcal mol^{-1}	
	gas phase	solution in acetonitrile	gas phase	solution in acetonitrile
I	3.00	4.46	0.0	6.4
I-a	0.91	1.35	6.9	12.6
II-e	13.64	19.40	2.0	0.1
II-z	13.86	19.72	1.9	0.0
III	12.05	17.44	–	–
IV	4.78	7.84	–	–

The value of b_μ is the most interesting characteristics of the molecule among those used for estimation of nonlinear optical properties of a solution polarized in external electric field.

The zwitter-ions, owing to their large dipole moments, should be oriented parallel to the electric field vector. Formation in solution of nonpolar molecular pairs prevents this orientation. At the antiparallel orientation of the two dipole moments, each molecular pair loses the first hyperpolarizability and polarization of the solution with external electric field is significantly reduced. The dimerization process to some extent is inhibited by a high electric field.

To promote to the coaxial or parallel orientation of molecular dipoles at their electrostatic attraction, an active molecules can be included into the polymer (see Ch. 8 in [6]), surrounded with nano-rings[2], captured by transparent organic cavitands (see section 4.2.3.4 in the book [9])[3], or attached with the polyatomic spatially extended groups. Of interest are also the Diels–Alder reaction, by which one can try to get a structure similar to tris-adduct, 2,3,5,6,7,8-hexamethylidenbicyclo[2.2.2]octane shown in Fig. 1. Obviously, the yield of adducts with the necessary electro-optical properties in the Diels–Alder reaction should increase at subjecting the reaction mixture to the action of electric field.

When capturing a proton, molecule **I** and zwitter-ions **II** are converted into cation **II**·H^+, where we found two local energy minima corresponding to the prototropic tautomers **II-e**·H^+ and **II-z**·H^+. The energy of **II-z**·H^+ is below the energy of **II-e**·H^+ by 0.3 kcal mol^{-1} in a vacuum, and by 0.2 kcal mol^{-1} in acetonitrile. Equilibrium structural parameters of tautomers **II-e**·H^+ and **II-z**·H^+ differ significantly only in the region of the N–H···N hydrogen bond (Table 1).

As show our calculations, the affinity of the molecule **I** to the proton in gas phase is by 4 kcal mol^{-1} higher than the affinity of 1,8-bis(dimethylamino)naphthalene. This value agrees with the data of [2]. For zwitter-ions **II**, this difference is less by the amount of

Table 3. Wavelengths and oscillator strengths of electronic transitions $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ in the zwitter-ions calculated by the TD PBE0/cc-pV (D, T)Z method

Zwitter-ion	Wavelength, nm		Oscillator strength[a]	
	gas phase	solution in acetonitrile	gas phase	solution in acetonitrile
II-e	327	323	0.154 (0.172)	0.206 (0.228)
	313	312	0.126 (0.128)	0.161 (0.165)
II-z	339	330	0.119 (0.134)	0.175 (0.194)
	315	314	0.138 (0.143)	0.172 (0.177)
III	332	326	0.145 (0.160)	0.199 (0.218)
	315	312	0.126 (0.130)	0.161 (0.166)

[a] The oscillator strengths are obtained using the transition dipole moments and (in parentheses) transient pulses. Both of long-wavelength singlet–singlet transitions belong to the π → π* type, and are polarized in the *xy* plane of naphthalene rings: $S_0 \rightarrow S_1$ along the C^9–C^{10} bond (*x*) and $S_0 \rightarrow S_2$ along the “long” *y* axis b.

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[2] Notable examples of nano-rings are cyclodextrins and macrocyclic polyethers composed of rotaxanes and catenanes [9].

[3] Transparent, stable and chemically inert hollow siloxane clusters, similar to silsesquioxanes $(RSiO_{1.5})_n$ could also serve as the cavitands. The proper choice of the R groups at silicon atoms can provide a good solubility of the nanocages with a captured molecule in a particular solvent.

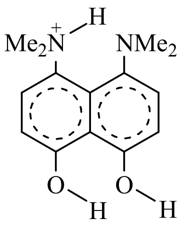
Table 4. Principal values of the polarizability tensor (α_1, α_2, α_3), average polarizability (α_{av}), optical anisotropy (δ^2), norm of the hyperpolarizability vector (| b|) and its projection (b_μ), a.u.

Molecule	α_1	α_2	α_3	α_{av}	δ^2, %	|b|	b_μ
Gaseous phase							
II-e	232	214	101	183	10	980	978
II-z	232	215	101	183	10	973	972
III	243	223	111	192	9	902	898
V[a]	144±2	120±3	54	106	13	856±35	–619±232
m-NA[b]	122	105	44	90	14	396	–347
Solution in acetonitrile							
II-e	311	306	129	249	12	1571	1554
II-z	310	308	129	249	12	1602	1602
III	331	321	145	266	10	1763	1711

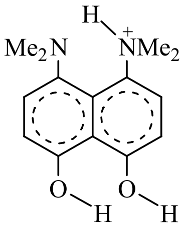
[a] **V** is the vanillin benzoid tautomers [8]. [b] *m*-NA is *m*-nitroaniline.

the energy of tautomeric transformation, that is, by 2 kcal mol^{-1}.

Along with **II-e**·H$^+$ and **II-z**·H$^+$ zwitter-ionic tautomers **II,** we investigated the structure and properties of heterocyclic zwitter-ion **III**, which is obtained from **II-e** and **II-z** by replacing the BH_2^+ cation for the labile proton between the nitrogen atoms.

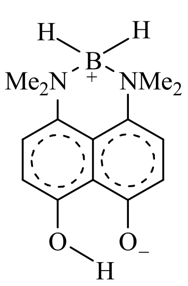


(**II-z**)· H$^+$

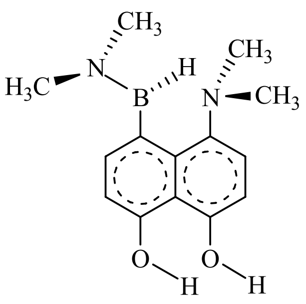


(**II-e**)· H$^+$

The adduct of BH_2^+ cation with 1,8-bis(dimethylamino)naphthalene, kindred to zwitter-ion **III,** was obtained and studied in [10,11].



III



IV

The equilibrium internuclear distances N^1–B and N^8–B in hypothetical zwitter-ion **III** Å are the same with the accuracy of 0.002 Å. Its dipole moment, polarizability and first hyperpolarizability (Table 4) differ little from the corresponding characteristics of zwitter-ions **II**, but there are significant structural peculiarities.

One of the boron-hydrogen bonds B–H' in the zwitter-ion **III** is adjacent to the plane near which are localized the nuclei of atoms of the naphthalene core, nitrogen and oxygen, while another bond, B–H'', is almost orthogonal to this plane. Therefore, the equilibrium configuration of **III** is asymmetric, and the

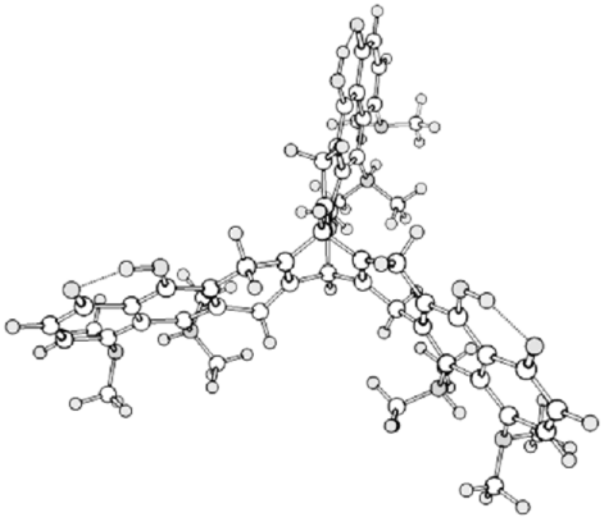


Fig. 1. One of the prototropic tautomers of the hypothetical Diels–Alder adduct, comprising zwitter-ionic fragments.

Table 5. Atomic charges q_A and valence V_A in the boron-containing isomers **III** and **IV**

Atom	Zwitter-ion **III**		Molecule **IV**	
	q_A, a.u.	V_A, a.u.	q_A, a.u.	V_A, a.u.
Gaseous phase				
B^8	0.23	3.37	0.56	3.24
N^1	–0.47	3.42	–0.71	3.12
N^8	–0.47	3.42	–0.50	3.26
O^4	–0.69	1.99	–0.69	1.94
O^5	–0.72	1.93	–0.72	1.91
H^4	0.48	0.77	0.50	0.76
H^5	–	–	0.49	0.77
Solution in acetonitrile				
B^8	0.22	3.37	0.51	3.31
N^1	–0.47	3.41	–0.72	3.09
N^8	–0.47	3.41	–0.48	3.33
O^4	–0.73	1.92	–0.72	1.91
O^5	–0.80	1.82	–0.72	1.91
H^4	0.48	0.78	0.50	0.75
H^5	–	–	0.51	0.74

proton transfer from the hydroxy group to the adjacent O atom transforms this zwitter-ion into its enantiomer. Here we encounter an example of a true degenerate tautomerism, in which two equivalent tautomers differ by the absolute configurations (Fig. 2).

The energy barrier separating the enantiomers of compound **III** is very low (0.5 kcal mol^{-1} relative to the minimum) and disappears at accounting for the "zero" vibrations in the harmonic approximation.

A similar proton transfer along the line of the intramolecular hydrogen bond, when the transitional structure has a second order symmetry axis passing through the labile proton, would leave the molecule unchanged. The quasi-degenerate tautomerism in this case can be achieved by asymmetric isotopic substitution, for example, by replacing one of the two ^{16}O nucleus nuclei in the hydrogen bond by ^{17}O. Energy of "zero" vibrations in these tautomers differ little. The difference in the energy and properties of the tautomers is even smaller if we replace one of the two ^{16}O nuclei in the hydrogen bond by the "shape isomer" [12].

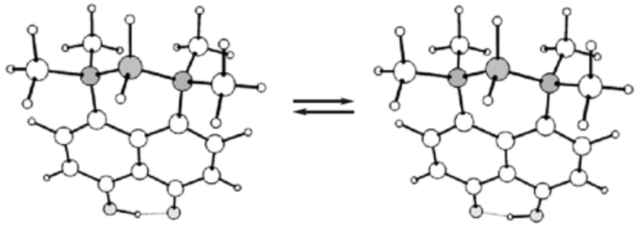


Fig. 2. Degenerate prototropic tautomerism of the zwitter-ion **III**.

The heterolytic cleavage of the B–H'' bond with the proton transfer to the oxygen atom O^- of the hydroxy group deprotonated in the zwitter-ion, according to the results of quantum-chemical calculation, is accompanied by the opening of the heterocycle, the conversion of zwitter-ion **III** in low-polar molecule **IV,** and the release of 20 kcal mol^{-1}. The remaining B–H' bond located in the mentioned plane of the zwitter-ion **III** is orthogonal to the plane of the molecule **IV**.

The bond B–N^1 in molecule **IV** is by 0.17 Å shorter than the bonds B–N^1 and B–N^8 in the zwitter-ion **III**. Its equilibrium length is 1.425 Å, that is, close to the average value of XRD bond lengths B–N 1.40 Å and 1.43 Å in the crystalline (dimethylamino)dimethylborane [13]. The equilibrium internuclear distance B–N^8 of 2.144 Å is shorter than the N^1–N^8 distance in the zwitter-ion **III**, but longer than the covalent boron–nitrogen bond.

The characteristics of the valence states of boron, nitrogen, oxygen, and labile hydrogen atoms in compounds **III** and **IV** are their charges q_A and valence V_A. These values (Table 5) are associated with the mathematic expectation and variance of the atomic electrons [14]:

$$q_A = Z_A - \Sigma_{a\in A}\lambda_a, \tag{3}$$

$$V_A = 2\Sigma_{a\in A}(\Delta\lambda_a)^2, \tag{4}$$

$$\lambda_a = <\psi_a|\boldsymbol{\rho}|\psi_a>, \tag{5}$$

$$(\Delta\lambda_a)^2 = <\psi_a|(\boldsymbol{\rho} - \lambda_a)^2|\psi_a> = <\psi_a|\boldsymbol{\rho}^2|\psi_a> - \lambda_a^2. \tag{6}$$

In formulas (3)–(6), Z_A is the charge of the nucleus of atom A; λ_a is thepopulation (average number of electrons) and $(\Delta\lambda_a)^2$ is the variance of the number of electrons in the one-electron state, as given by the orthogonalized hybrid (natural) nuclear spin-orbital ψ_a. The core of the integral operator $\boldsymbol{\rho}$ is a one-electron *density matrix* $\rho(r\sigma|r'\sigma')$. The natural atomic orbitals contributing to the spin-orbital ψ_a are determined according to [15].

The boron atom in zwitter-ion **III** has a positive charge, its valence is 3.37, the indices of chemical bonds with nitrogen atoms are 0.633 (B–N^1) and

0.637 (B–N^8) and with hydrogen atoms, 0.975 (B–H') and 0.970 (B–H''). All these quantities are insensitive to the effects of the polarizable medium. In molecule **IV** the charge on the boron atom is higher, while the valence is a bit less. The indices of the bonds B–N, B–H, and B–C are close to unity: 1.01, 0.94 and 0.88, respectively, in the free molecule, 0.95, 0.94 and 0.88, respectively, in the solution.

Charges on nitrogen atoms (tetra-coordinated in zwitter-ion **III** and tri-coordinated in molecule **IV**) when the valence is $V > 3$ were found to be negative. In the zwitter-ion the oxygen atom O slightly exceeds the hydroxy oxygen atom by the absolute value of the charge.

Thus, according to the results of quantum-chemical calculations the coexistence of several prototropic tautomers of 4,5-dihydroxy-1,8-bis(dimethylamino)naphthalene is possible. In the gas phase the preferred by energy is the low-polar molecule with one asymmetric intramolecular hydrogen bond O–H···O. In a polarizable medium, in particular, in acetonitrile, dominates a pair of similar by energy zwitter-ionic tautomers with asymmetric intramolecular hydrogen bonds O–H···O and N–H···N. These zwitter-ions and similar hypothetical heterocyclic zwitter-ion with the cation BH_2^+ instead of the labile proton between the amino groups are interesting not only as a Brønsted bases, but also as a high polar molecules with non-linear electro-optical properties.

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