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Quantum Chemical Study of Tautomerism of Bullvalene, Bullvalenol, and the Corresponding Ketone

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Abstract—Using the quantum chemical method PBE0/cc-pVTZ, we determined structural parameters and dipole moments of bullvalene (tricyclo[3.3.2.$0^{4.6}$]deca-2,7,9-triene), 1-, 2-, 3-, and 4-hydroxytricyclo[3.3.2.$0^{4.6}$]-deca-2,7,9-trienes, and isomeric 2- and 3-ketones transforming into each other through the keto-enol tautomerism and Cope rearrangement with the triatomic ring migration. The dominant tautomer is 3-ketone containing a triatomic ring conjugated with the carbonyl group.

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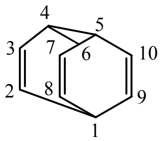
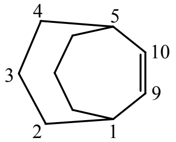
Bullvalene (tricyclo[3.3.2.$0^{4.6}$]deca-2,7,9-triene)[1] has been synthesized in 1963 by Schroeder [1] soon after the W. Döring's prediction [2] of extremely interesting structural and dynamic features of this hydrocarbon due to the easy Cope rearrangement [4] and the symmetry of the molecule. The concept about the degenerate valence tautomerism which is inherent to the bullvalene molecule [5] is not consistent with the usual definition of tautomerism as a fast and reversible struc-tural isomerization, since at the Cope rearrangement of unsubstituted isotopically uniform bullvalene the energy, equilibrium configuration, and structural formula of the molecule remain unchanged.

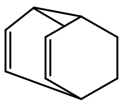
The replacement of certain atomic nuclei by isotopes or isomers (the metastable excited nuclei) as well as the replacement of some atoms by isovalent atoms of other chemical elements or radicals can reduce the symmetry of the molecule, so that the tautomers become distinguishable, but their energies remain the same. In [6] the concept of degenerate tautomerism was associated with the chirality of the tautomers. The degenerate tautomers differ in absolute configuration, but in the case of C_{3v} point group the enantiomeric configurations are impossible.



S_0



$S_{\cap}$; T_1



T_2

However, despite the fact that the tautomers are not distinguishable, the phenomenon of rapid and reversible formation and breaking of carbon–carbon bonds in the bullvalene molecule has been studied and proven by NMR. The low-temperature proton magnetic resonance spectrum of bullvalene at –85ºC consists of two groups of signals with a ratio of integral intensities 6:4, while its high-temperature spectrum consists of a only signal (1.5 Hz), which indicates the magnetic equivalence of the bullvalene protons at the temperatures above 100ºC [1–3]. The concerted motion of the carbon and hydrogen atomic nuclei in this molecule at sufficiently high temperatures causes averaging of the chemical environment of all hydrogen and all carbon nuclei. Therefore the experimentally observed chemical shift of ^{1}H signal in NMR spectrum at high temperature is equal to the weighted average of the signals in the low-temperature spectrum [3].[2]

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[1] Both names were taken from the original papers [1–3]. The carbon atom bound to two exocyclic atoms in all structural formulas of the bullvalene derivatives is marked by letters (CH_2).

[2] In the rigid and highly symmetrical (D_{5h}) pentaprizmane molecule, which is the isomer of bullvalene , all ten C atoms and all ten hydrogen atoms are equivalent, but its ^{1}H and ^{13}C NMR spectra [7] differ from those of bullvalene [3].

Table 1. Calculated shielding constants (σ) and chemical shifts (σ–σ_{av}) in the ^{1}H and ^{13}C NMR spectra of unsubstituted bullvalene, ppm

Nucleus	σ	σ–σ_{av}[a]	Nucleus	σ	σ–σ_{av}[a]
H^1	29.53	2.47 (2.14)	C^1	154.47	56.06 (55.5)
H^2	25.49	–1.57 (–1.43)	C^2	55.39	–43.02 (–41.5)
H^3	25.43	–1.63 (–1.43)	C^3	55.29	–43.12 (–41.5)
H^4	29.45	2.39 (2.14)	C^4	165.85	67.44 (–64.5)
H (σ_{av})	27.06	–	C (σ_{av})	98.41	–

[a] Numbers in parentheses correspond to the experimental low-temperature ^{1}H [3] and ^{13}C [10] NMR spectra.

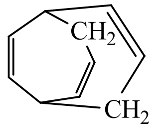
The presence of only two groups of 1H NMR signals in the low-temperature spectrum, that is, the coincidence of chemical shifts of the protons in the triatomic ring with that of the H^1 nucleus located on the symmetry axis of the molecule could be taken as a proof of the mutual transformation of some tautomers also at –85ºC. However, it was suggested in [3] that the proton signal of H^1 of bullvalene is shifted relative to the signal of the proton H^1 in a similar structural fragment of the barrelene (bicyclo[2.2.2]octa-2,5,7-triene) $HC(CH=CH)_3CH$ [8] due to the influence of the triatomic ring, and represents the superposition of proton signals at the triatomic ring.

This assumption is supported by the results of quantum chemical calculations of screening constants that we performed by the PBE0/cc-pVTZ method using the GAUSSIAN-03 software [9]. The calculated chemical shifts of the proton H^1 and the protons of triatomic ring relative to the weighted average value σ_{av} are virtually identical. However, chemical shifts in the ^{13}C NMR spectrum of the C^1 nucleus and the carbon nuclei of triatomic ring are different (Table 1).

Equilibrium internuclear distances in the bullvalene molecule ground state S_0 is close to the data lengths of chemical bonds in the crystal known from XRD (Table 2). The absence in the vibrational spectrum of imaginary frequencies of harmonic vibrations suggests that the calculated equilibrium structure (S_0) with C_{3v} symmetry corresponds to the energy minimum. The small dipole moment 0.55 D disappears when averaged over 1 209 600 equivalent equilibrium nuclear configurations of the molecule.

The activation energy for the opening of triatomic ring of bullvalene equals 13.4 kcal mol^{-1}. This value is determined as a height of the saddle point $S_\cap$, characterized by a single imaginary wave number i394 cm^{-1} in the vibrational spectrum over the energy minima with taking into account the zero-point correction of structures $S_\cap$ and S_0. The value of the activation energy is in the an agreement with the experimental estimates (11.7±0.2 [12], 11.8±1.0 [13], 12.8±0.1 [14], 13.1 [12, 15] and 14.3 kcal mol^{-1} [16]). In the Slater determinants approximating the singlet multielectron wave functions Ψ_0 and $\Psi_\cap$, the spin polarization of the orbitals is not detected.

In the equilibrium structure of 2,3,4,6,7,8-dehydrobicyclo[3.3.2]dec-9-ene ($S_\cap$), which determines the activation energy for the bullvalene tautomeric transformation, the distance between two atoms of the triatomic ring increases to 2.019 Å. This value is significantly less than the corresponding internuclear distance 2.517 Å in the bicyclo[3.3.2]deca-2,6,9-triene ($C_{10}H_{12}$). The structure $S_\cap$ differs little from the equilibrium structure of the triplet excited state (T_1) corresponding to the minimum energy of a molecule with the open triatomic ring. The symmetry of both the ($S_\cap$) and (T_1) structures is C_{2v}. The difference in the lengths of the carbon–carbon bonds is 0.026 Å or less and of the carbon–hydrogen bonds, 0.006 Å or less (Table 2). However, the energy of the T_1 state is by 24.1 kcal mol^{-1} higher than the energy of the $S_\cap$ state and by 37.5 kcal mol^{-1} higher than that of the ground state S_0.



$C_{10}H_{12}$

The energy of the triplet state T_2, which occurs at the degradation of the double bond C^2=C^3, is more higher (60.0 kcal mol^{-1} relative to S_0). So high energy value of the 2,3-biradical is due to the conservation of the bullvalene tricyclic structure, which prevents to occur the spatial remoteness of the unpaired molecular orbitals localized on the atoms C^2 and C^3. The equilibrium bond length C^2–C^3 in the region of localization of the triplet excitation increases to 1.453 Å, the dihedral angle $C^1C^2C^3C^4$ is equal to 45.0º, being less than the dihedral angles in the equilibrium triplet states of normal olefins [17, 18].

Table 2. Equilibrium internuclear distances (Å) in structures S_0, $S_{\cap}$, and T_1 of bullvalene, anions **Ia,** and ketones **II**

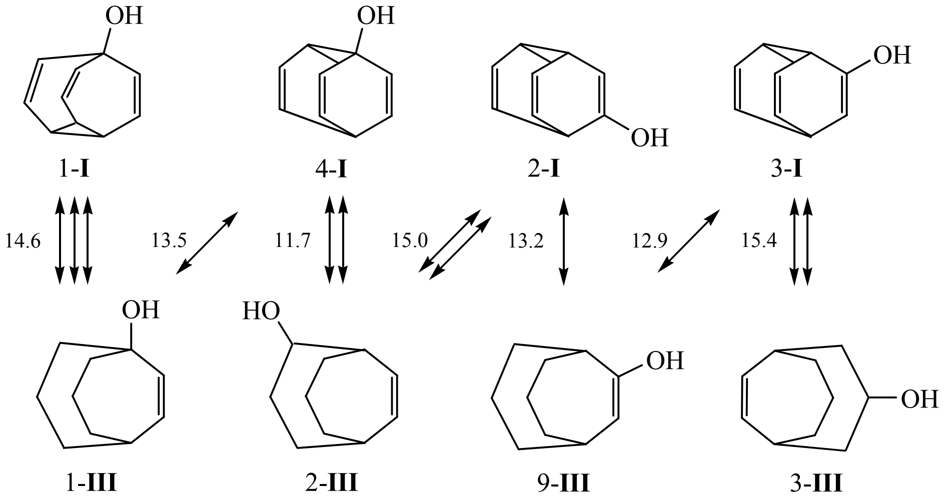
Bond[a]	S_0[b]	$S_{\cap}$	T_1	1-**Ia**	2-**Ia**	3-**Ia**	4-**Ia**	2-**II**	3-**II**
1–2	1.509 (1.51)	1.493	1.509	1.544	1.564	1.508	1.498	1.517	1.529
1–8	1.509 (1.51)	1.493	1.509	1.544	1.500	1.510	1.509	1.507	1.506
1–9	1.509 (1.51)	1.490	1.516	1.544	1.500	1.510	1.501	1.509	1.506
2–3	1.333 (1.33)	1.384	1.378	1.336	1.390	1.383	1.358	1.518	1.515
3–4	1.465 (1.45)	1.384	1.378	1.470	1.462	1.519	1.449	1.505	1.481
4–5	1.523 (1.54)	1.493	1.509	1.524	1.536	1.518	1.525	1.500	1.515
5–6	1.523 (1.54)	1.493	1.509	1.524	1.528	1.540	1.512	1.500	1.515
6–7	1.465 (1.45)	1.384	1.378	1.470	1.461	1.463	1.382	1.468	1.468
7–8	1.333 (1.33)	1.384	1.378	1.336	1.337	1.336	1.387	1.332	1.332
9–10	1.333 (1.33)	1.324	1.324	1.336	1.337	1.336	1.328	1.332	1.332
5–10	1.465 (1.45)	1.490	1.516	1.470	1.461	1.463	1.498	1.469	1.468
4–6	1.523 (1.54)	2.019	2.527	1.524	1.537	1.518	2.363	1.545	1.528
CO	–	–	–	1.325	1.253	1.262	1.237	1.206	1.211

[a] The equilibrium internuclear distances CH are 1.082–1.096 Å. [b] The results of XRD analysis are in parentheses [11].

Electronic excitation of one of three bridges between the triatomic ring and the C^1 atom has little effect on the structure of the other two –CH=CH– bridges. The chemical bonds in them are coplanar with the accuracy up to 3°, the length of double bonds does not increase.

Four nonequivalent positions of hydrogen atoms in the equilibrium structure of the bullvalene molecule suggest the existence of four tautomers of hydroxybullvalene (**I**) and, taking into account the keto-enol tautomerism, of two oxo-tautomers (**II**). Relative energies and dipole moments of the six $C_{10}H_{10}O$ tautomers calculated by the quantum chemical methods PBE0/cc-pVTZ are shown in Table 3, the barriers to the triatomic ring opening, in the Schemes 1 and 2 (in kcal mol^{-1}).

Scheme 1.

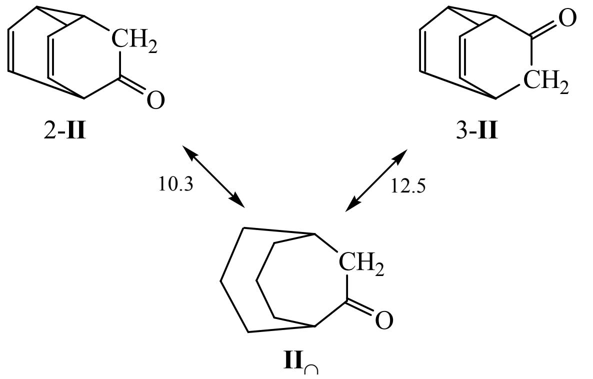


The lowest calculated energy was obtained for 3-oxo-tautomer, ketone 3-**II**, whose carbonyl group is conjugated with the triatomic ring. The energy of ketone 2-**II** is slightly higher and the relative energies of enols 2-**I,** 3-**I**, and tertiary alcohols 1-**I,** 4-**I** are above 13 kcal mol^{-1}. The mutual transformation of the two close by energy enol tautomers, 2-**I** and 3-**I,** the

Table 3. Dipole moments (μ, D) and relative energies (Δ*E*, kcal mol^{-1}) of alcohols **I** and ketones **II**

Alcohol	μ	Δ*E*	Ketone	μ	Δ*E*
1-**I**	1.95	15.5	–	–	–
2-**I**	1.30	13.2	2-**II**	3.26	2.2
3-**I**	2.10	13.5	3-**II**	3.14	0.0
4-**I**	1.19	16.5	–	–	–

Scheme 2.



migration of triatomic ring does not require rotation of upon the hydroxyl groups relative to the C–OH axis.

The lowest barriers for opening the triatomic rings in the $C_{10}H_{10}O$ molecules are obtained for the nondegenerate tautomeric conversion 2-**II** ↔ **II**$_{\cap}$ ↔ 3-**II** (Table 3). In the equilibrium structure **II**$_{\cap}$ corresponding to the saddle point energy, the internuclear distances of triatomic ring bonds to be cleaved in tautomer 2-**II** and 3-**II** are equal to 2.045 Å and 2.025 Å respectively. In the equilibrium structures **III** associated with the barriers of tautomeric transformations of hydroxybullvalene **I** the internuclear distances corresponding to the cleaved/formed C–C bonds are in the range 2.02–2.13 Å.

We can presume that at the ionization of the hydroxybullvalene or corresponding oxo-tautomer with a Brønsted base four anions are formed. Elimination of a proton from the methylene or hydroxy groups in the dominant ketone 3-**II** and enol 3-**I** respectively results in the formation of the anion 3-**Ia**, from ketone 2-**II** or enol 2-**I** – anion 2-**Ia**, from enol 1-**I** – anion 1-**Ia**. Removing the proton from the hydroxyl group connected directly with the triatomic ring leads to the opening of the latter. The length of one of its two bonds adjacent to the $C–O^-$ increases to 2.363 Å, while the other remains short (1.525 Å). As a result, the 4-hydroxybullvalene 4-**I** is transformed into bicyclic anion 4-**Ia** with delocalized charge.

The equilibrium carbon–oxygen bond length in anions **Ia** is longer than in ketones **II**, but shorter than in enol **I**. It increases with the increasing energy of the anions in a series of tautomers 2-**Ia** < 4-**Ia** <3-**Ia** < 1-**Ia**. For non-ionized enols we obtained a different relationship of the relative energies: 2-**I** < 3-**I** < 1-**I** < 4-**I**, while for the isoelectronic fluorobullvalene we found that the highly symmetrical structure 1-F-**I** was the preferred one**.** This structure is associated with the lowest energy calculated for the series of tautomers: 1-F-**I** < 3-F-**I** < 2-F-**I** < 4-F-(**I**).[3]

It is known that the Brønsted bases promote the Cope rearrangement of 3-hydroxy-1,5-diene [20–22]. The reaction rate in the presence of potassium hydride increases 10^{10}–10^{17} times [20]. Therefore, the absence of tricyclic equilibrium structure and very low activation barrier of the Cope rearrangement in the case of 4-**Ia** anion is not unexpected. Equilibrium lengths of chemical bonds in the equilibrium structures **IIIa** corresponding to saddle points of energy of $C_{10}H_9O^-$ anions, are given in Table 4.

Replacing the hydrogen atoms in the bullvalene bicyclic structure $S_{\cap}$ by oxygen atom (O^-) leads to four anionic structures of **IIIa**. Structure 1-**IIIa** corresponds to anion 1-**Ia**, the optimal structure 2-**IIIa** to anions 2-**Ia** and 4-**Ia**, structure 3-**IIIa** to anion 3-**Ia**, structure 9-**IIIa** to anions 2-**Ia** and 3-**Ia**, which are formed at removing the proton from the methylene group of the dominant 2- and 3-oxo-tautomers or from the hydroxyl group of 2- and 3-hydroxy-tautomers of the bullvalene, respectively. Note that it is a minor difference between the structures 2-**IIIa** and 4-**Ia**.

The activation energy of the rearrangement of anion **Ia** is defined as the height of the saddle point **IIIa** over the minimum energy **Ia**, corrected by accounting for the difference between the zero-points of the structures **IIIa** and **Ia**. The calculated activation energies in kcal mol^{-1} are shown in Scheme 3. In all cases trajectories (IRC) were calculated connecting the saddle point with the corresponding minimum. The structure of 3-**IIIa** can be called a tetracyclic, but two triatomic rings in

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[3] Energy preference of 1-fluorobullvalene is confirmed by ^1H NMR spectra [19].

Table 4. Equilibrium internuclear distances (Å) in structures **II**$_{\cap}$, **III**, and **IIIa** corresponding to the energy saddle points of the molecules $C_{10}H_{10}O$ and anions $C_{10}H_9O^-$

Bond	**II**$_{\cap}$	1-**III**	2-**III**	3-**III**	9-**III**	1-**IIIa**	2-**IIIa**	3-**IIIa**	9-**IIIa**
1–2	1.493	1.492	1.488	1.496	1.491	1.537	1.547	1.521	1.491
1–8	1.493	1.492	1.497	1.490	1.491	1.537	1.508	1.487	1.491
1–9	1.501	1.489	1.490	1.489	1.494	1.517	1.495	1.475	1.541
2–3	1.380	1.387	1.394	1.388	1.385	1.378	1.417	1.451	1.387
3–4	1.386	1.379	1.372	1.382	1.382	1.398	1.403	1.451	1.384
4–5	1.487	1.494	1.494	1.494	1.493	1.492	1.483	1.521	1.501
5–6	1.487	1.494	1.498	1.491	1.493	1.492	1.505	1.487	1.501
6–7	1.386	1.379	1.374	1.382	1.382	1.398	1.412	1.437	1.384
7–8	1.380	1.387	1.389	1.386	1.385	1.378	1.360	1.437	1.387
9–10	1.508	1.323	1.325	1.324	1.326	1.328	1.329	1.330	1.374
5–10	1.511	1.491	1.494	1.490	1.490	1.490	1.485	1.475	1.490
C–O$^-$/C=O	1.207	1.409	1.363	1.375	1.363	1.316	1.245	1.251	1.259
O–H	–	0.960	0.960	0.959	0.958	–	–	–	–
$i\nu_{\cap}$[a]	–357	–367	–300	–418	–386	–427	–379	–207	–391

[a] $\nu_{\cap}$ is imaginary wave number in the vibrational spectrum, cm^{-1}.

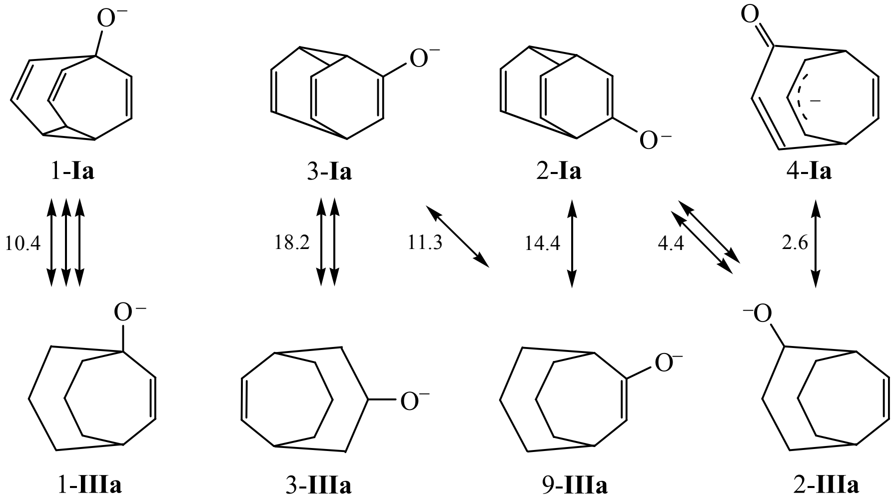
its composition include the stretched bond with the length 1.67 Å. Other structures of **IIIa** are bicyclic with the lengths of broken bonds of the opened triatomic ring within 1.91–2.40 Å.

A very low activation energy in the cases of 2-**Ia** and 4-**Ia** and relatively high one in the case of 3-**Ia** is of interest taking into consideration a small difference in the relative energies of the anions: 2-**Ia** 0.0, 4-**Ia** 1.8, and 3-**Ia** 3.1 kcal mol^{-1}. The highly symmetrical structure of anion 1-**Ia** is unfavorable by energy (20.8 kcal mol^{-1}).

Our results are consistent with the experimentally established fact that all ten hydrogen atoms are replaced by deuterium at the interaction of $C_{10}H_{10}O$ with heavy water in the presence of 0.1 N alkali and with the assumption that the dominant tautomer is 3-**II** [12]. The inclusion of an oxygen atom in the fluctuating structure of bullvalene significantly accelerates the process of its valence isomerization in alkaline medium, since the activation energy of the triatomic ring opening in some oxide-anionic tautomers practically disappears. Due to the energy preference of ketones in comparison with hydroxy-tautomers, the protonation of the oxide anions leads to the domination in the tautomeric mixture of a pair of non-equivalent oxo-tautomers.

The results of the quantum chemical study of tautomerism of bullvalene $C_{10}H_{10}$ and its oxygen-containing derivatives $C_{10}H_{10}O$ and $C_{10}H_9O^-$ presented in this report supplement the previous study of the

Scheme 3.



mechanism of Cope rearrangement in the case of the nonstrained and free (not included in the polycyclic system) hexa-1,5-diene [23, 24].

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