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Quantum-Chemical Study of Barbaralone in Singlet and Triplet States

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Abstract—Equilibrium structural parameters of barbaralone molecule in the S_0, T_1, and T_2 states have been determined by DFT (U)PBE0/cc-pVTZ method. The calculated barrier of the Cope rearrangement in the singlet state (9.4 kcal/mol) was close to the experimental activation energy. The equilibrium structure in the T_1 state (29.3 kcal/mol) was similar to the $S_\cap$ intermediate structure. The $S_0 \rightarrow T_2$ excitation (69.2 kcal/mol) was accompanied by extension of the carbon–oxygen bond (1.207 Å → 1.284 Å) and decreasing the molecule dipole moment (3.51 D → 2.77 D).

Keywords: barbaralone, structure, symmetry, Cope rearrangement, activation energy, triplet state, bullvalene, pentaprismane, asterane

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Barbaralone C_9H_8O (Fig. 1) has been prepared by Doering et al. [1] and has been used in the optimized synthesis of bullvalene [2]. The NMR spectra have showed the structural fluctuation of barbaralone molecule via the Cope rearrangement [1–7].

In this work we simulated equilibrium structural parameters of barbaralone molecule in the ground singlet S_0 as well as in two excited triplet T_1, and T_2 states using the DFT (U)PBE0/cc-pVTZ method; furthermore, the parameters of the transition states ($S_\cap$ and $T_\cap$) were found, governing the Cope rearrangement in the singlet and the triplet states. Vibration spectra were simulated for all equilibrium structures in the harmonic approximation.

Group	Operations	Group
C_{2V}	$E \leftrightarrow E$ $C_2^z \leftrightarrow R$ $\sigma^{yz} \leftrightarrow \sigma^{yz}$ $\sigma^{xz} \leftrightarrow \sigma^{yz} R$	C_SR

The equilibrium interatomic distances in the singlet barbaralone reflected the conjugation of the C=C and C=O double bonds with the three-membered cycle (Table 1). The labile bond cleaved in the course of the Cope rearrangement was 0.032 Å longer than the other two carbon–carbon bonds in the three-membered ring. The carbonyl group atoms and the adjacent carbon atoms were located in the symmetry plane of the molecule. The calculated energy barrier of the singlet barbaralone rearrangement ($\Delta E_\cap$ 9.4 kcal/mol) was within the range of the experimentally determined activation energy (8.1–11.5 kcal/mol [4, 5]).

The rearrangement of the singlet barbaralone combined with an appropriate rotation of the molecule as a whole retained the atoms coordinates unchanged. That internal symmetry operation (R) supplemented the C_S point symmetry group of barbaralone to the C_SR group (the designation being similar to that suggested in [8] for fluctuating group of cyclohexane). The latter one is isomorphic to the C_{2V} symmetry group of the transition structure $S_\cap$. The operations of C_{2V} point symmetry group and the C_SR group arre in the one-to one correspondence. (Standard notation of the point symmetry group operations is used).

Rearrangement of barbaralone may be considered as degenerate; however, the using of the widespread terms “degenerate tautomerism” and “valence isomerism” are not correct if the cleavage of chemical bonds and their formation (including the increase in multiplicity) result in a structure identical to that of the starting molecule [9–11].

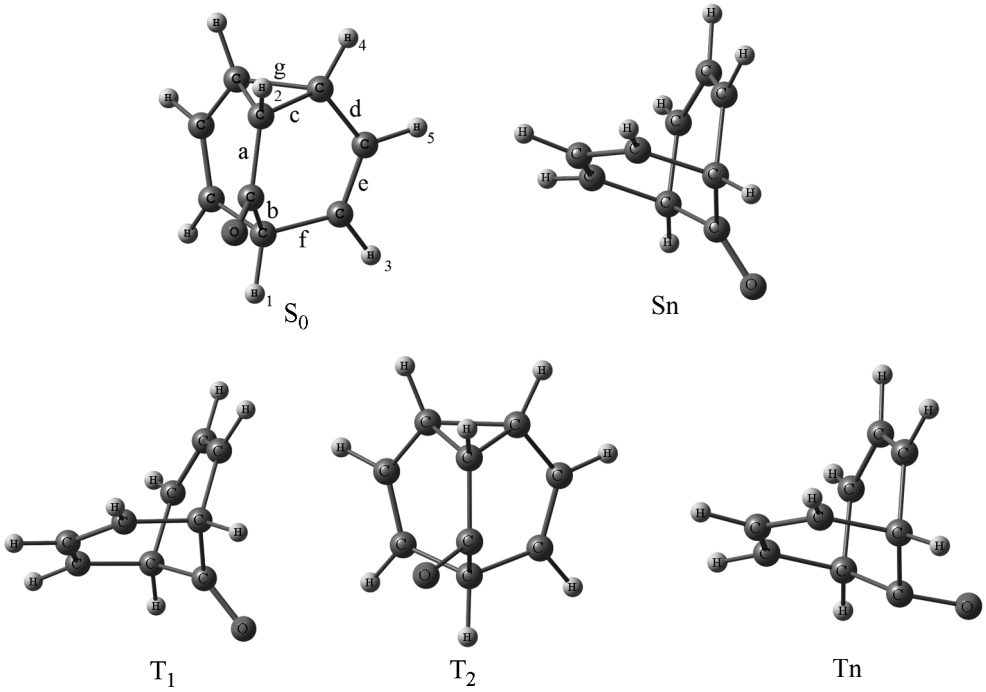

Fig. 1. Equilibrium configurations of singlet and triplet barbaralone.

Parameters of simulated ^{1}H and ^{13}C NMR spectra of barbaralone and the relative compounds asterane and bullvalene (Fig. 2) are presented in Table 2. The chemical shifts δ were determined as the difference between the shielding constants σ: $\delta = \sigma_{ref} - \sigma$, the reference being tetramethylsilane with the simulated shielding constants of 31.57 ppm (^{1}H) and 189.07 ppm (^{13}C).

The low-temperature (*lt*) ^{1}H NMR spectrum of barbaralone consisted of five signals. Two of them

Table 1. Equilibrium structural parameters of barbaralone molecule

Bond, angle	S_0 (C_S)	$S_\cap$ (C_{2V})	T_1 (C_{2V})	T_2 (C_1)	$T_\cap$ (C_S)
Interatomic distance, Å					
CO	1.207	1.206	1.197	1.284	1.278
a	1.475	1.494	1.522	1.484	1.532
b	1.519	1.494	1.522	1.565	1.532
c	1.511	1.495	1.508	1.499; 1.509	1.480; 1.485
d	1.466	1.382	1.381	1.455; 1.455	1.381; 1.381
e	1.333	1.382	1.381	1.337; 1.338	1.381; 1.381
f	1.513	1.495	1.508	1.496; 1.499	1.480; 1.485
g	1.543	1.979	2.526	1.581	2.093
Bond angle at the carbonyl carbon, deg					
a^CO	124.1	123.6	124.6	118.8	116.5
b^CO	122.9	123.6	124.6	115.1	116.5
a^b	113.0	112.8	110.8	110.9	109.0

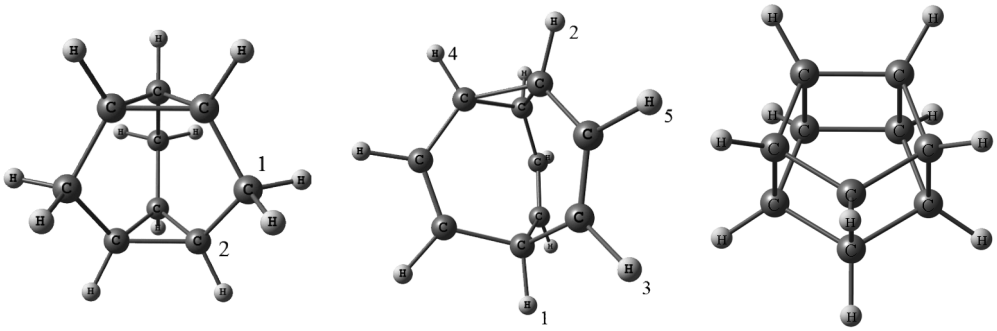

Fig. 2. Equilibrium configurations of asterane, bullvalene, and pentaprismane molecules.

merged in the experimental spectrum [4] to give a single strong signal of four protons at the double bonds. The weight-average chemical shift of the protons at the three-membered barbaralone ring (2.40 ppm) was more downfield than the chemical shift of protons at the three-membered rings of bullvalene (2.12 ppm) and especially of asterane (0.51 ppm). The chemical shifts of equal intensity corresponding to the proton at the three-membered ring and the methylene proton simulated for the symmetrical (D_{3h}) asterane molecule were close to those in the experimental spectrum [12].

The high-temperature (*ht*) barbaralone spectrum contained three signals with the intensities ratio of 1 : 2 : 1. The chemical shift of the stronger signal (4.39 ppm) resulted from the averaging of the chemical shifts of H^3 and H^4 protons, whereas the chemical shift of 2.71 ppm was an average of those of H^1 and H^2. The temperature had no effect on the chemical shift of the H^5 proton. The experimental spectrum revealed only the weakening of the signals due to the shifting of the signal of the adjacent proton at the double bond. The temperature-induced changes of the simulated ^{13}C NMR spectrum were similar to those of the proton spectrum.

The NMR spectrum simulated for the transition structure included the chemical shifts of H^1 and H^2 (3.01 ppm), H^3 and H^4 (5.00 ppm), and H^5 (5.20 ppm). It was somewhat similar to the experimental ^1H NMR spectrum. Yet the identification of high-temperature state of the fluctuating molecule as that of the transition state is incorrect as becomes obvious after examination of the high-temperature NMR spectrum of bullvalene (Table 2). In the latter structure, each of the carbon atoms was similarly linked to the other nine carbon atoms, and all the protons were magnetically equivalent [13–15]. No configuration of the atoms in the three-dimensional space (including the highly symmetrical pentaprismane with the chemically equivalent atoms) (Fig. 2) satisfied these conditions [10]. The chemical shift simulated for pentaprismane was only by 0.02 ppm different from that of the experimentally determined [16] but it was by 1.05 ppm smaller than the simulated shift of the signal of the ten protons in the high-temperature spectrum of bullvalene. The simulated ^{13}C chemical shift in pentaprismane was by 1.0 ppm larger than the experimental one [16] and by 41.1 ppm smaller than the simulated shift of the signal of ten ^{13}C nuclei in the high-temperature spectrum of bullvalene.

In contrast to the unsubstituted bullvalene, transforming into the identical structure via the Cope

Scheme 1.

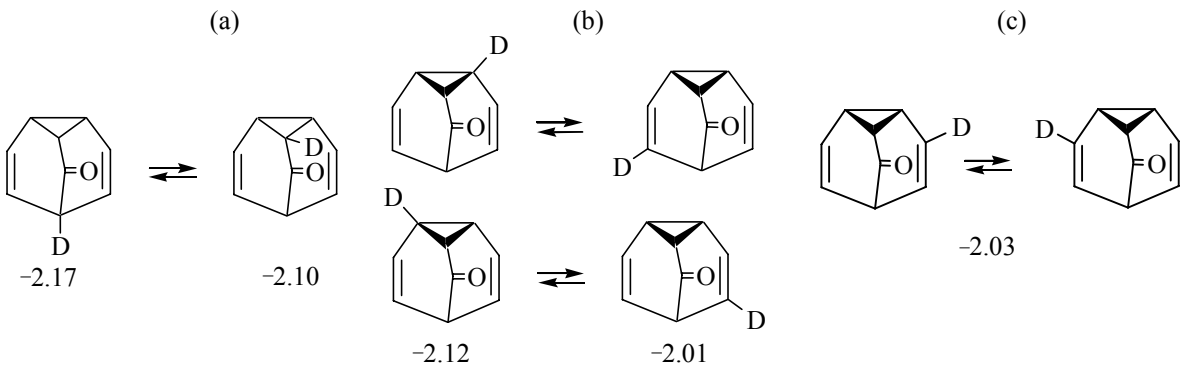

Table 2. Simulated shielding constants and chemical shifts at low (*lt*) and high (*ht*) temperature[a]

Compound	Nucleus position	Shielding constant	δ, ppm	
			lt	*ht*
		^{1}H NMR spectrum		
Barbaralone	1	28.66 (1)	2.91 (1)	2.71 (2)
	2	29.46 (1)	2.11 (1)	
	3	25.35 (2)	6.22 (2)	4.39 (4)
	4	29.02 (2)	2.55 (2)	
	5	25.62 (2)	5.95 (2)	5.95 (2)
Asterane	1	29.26 (6)	2.31 (6) [2.27]	
	2	31.06 (6)	0.51 (6) [0.60]	
Bullvalene	1	29.53 (1)	2.04 (1) [2.08]	
	2	29.45 (3)	2.12 (3) [2.08]	4.51 (10) [4.22]
	3	25.49 (3)	6.09 (3) [5.65]	
	4	25.43 (3)	6.14 (3) [5.65]	
Pentaprismane	1	28.12 (10)	3.46 (10) [3.48]	
		^{13}C NMR spectrum		
Barbaralone	1	135.0 (1)	54.0 (1) [49.9, 50.6]	58.3 (2)
	2	162.4 (1)	26.6 (1) [26.8, 26.9]	
	3	54.4 (2)	134.7 (2) [128.3, 129.0]	84.9 (2)
	4	154.0 (2)	35.1 (2) [33.1, 33.4]	
	5	61.8 (2)	127.3 (2) [121.5, 122.5]	127.3 (2)
Asterane	1	168.5 (6)	20.6 (6)	
	2	176.3 (6)	12.8 (6)	
Bullvalene	1	154.5 (1)	34.6 (1) [31.2]	
	2	165.8 (3)	23.2 (3) [21.1]	90.7 (10) [86.5]
	3	55.4 (3)	133.7 (3) [128.5]	
	4	55.3 (3)	133.8 (3) [128.3]	
Pentaprismane	1	139.5 (10)	49.6 (10) [48.6]	

[a] Relative intensities are given in parentheses, experimental chemical shifts [5, 6, 12–16] are given in brackets.

rearrangement, the isotopomers of the deuterated bullvalene-*d* were interconverted. The quasi degenerate tautomerism of achiral isotopomers (a), the quasi degenerate tautomerism of chiral isotopomers (b), and the degenerate tautomerism of chiral isotopomers (enantiomers) (c) could be distinguished (Scheme 1).

The energies of the isotopomers (relative to that of the unsubstituted bullvalene) in kcal/mol are given below the structures. The difference in the energies of isotopomers of bullvalene-*d* was due to the changed frequency of the normal vibrations and did not exceed 0.16 kcal/mol. The calculated difference in the enthalpies of the quasi degenerate achiral isotopomers (ΔH 0.09 kcal/mol) coincided with the experimental value (0.11 kcal/mol [17]).

The Cope rearrangement accompanied with the appropriate rotation of the molecule as a whole was an operation transforming the starting equilibrium nuclei configuration into its mirror. The "degenerate tautomerism" term used in the case of fast reversible interconversion of enantiomers is not the same as the "racemization." The latter means the transformation of a pure enantiomer (non-racemic substance) into the racemic state, with the molecules of the same

constitution. Such irreversible process based on the reversible interconversion of the enantiomers is accompanies with the loss of the optical activity of the substance [18]. In contrast to the degenerate tautomerism requiring retaining the constant molecule energy, the racemization of a pure enantiomer changes the free energy by $\Delta G^0 = -RT\ln 2$ (–0.4 kcal/mol at room temperature) [18].

The ambiguity of determination the symmetry of barbaralone molecule did not result in the ambiguity of its thermodynamic parameters. The "entropy of symmetry" of the oscillating structure $S_{sym} = -R\ln \sigma$ [18, 19] was compensated by the "mixing entropy" $S_{mix} = -R\Sigma W_i \ln W_i$ (the summation being run over the N states related via the intramolecular rearrangement with the states population of $W_i = 1/N$ and $N = 2$) upon the increasing symmetry number (i. e. the number of physically realizable symmetry operations) σ from 1 to 2.

The excitation of barbaralone into the lower triplet state T_1 (29.3 kcal/mol) was accompanied with the opening of the three-membered ring while preserving the double bond in the carbonyl group. The molecule structure in that state was similar to the $S_\cap$ structure (Fig. 1). However, the equilibrium distance between the nuclei of the cleaved bond g in the T_1 state was by 0.547 Å larger than that in the $S_\cap$ structure (Table 1). The mathematical expectation of the squared spin under the (U)PBE0 approximation $\langle S^2\rangle = 2.006$ *e* was close to the precise squared spin in the triplet state. The dispersion of the multi-electron spin in the equilibrium excited T_1, state {as calculated using the (RO)PBE0//(U)PBE0/cc-pVTZ method with natural population analysis of the atomic orbitals NPA [20, 21]} was primarily distributed between the four equivalent carbon atoms. Their total contribution into the $DS = \langle S^2\rangle - \langle S\rangle^2 = 1$ was 95%, only 3% was left for the carbonyl group.

Electron excitation of barbaralone molecule into the higher triplet state T_2 (69.2 kcal/mol) preserved the tricyclic carbon skeleton, being reflected primarily in the structural parameters of the carbonyl group. The equilibrium interatomic distance was increased from 1.207 Å (C=O) to 1.284 Å (C˙–O˙). The C_S symmetry of the equilibrium configuration of the ground singlet state was lost due to the deviation of the carbonyl carbon out of the plane where the adjacent carbon and oxygen atoms were located. Mathematical expectation of the squared spin in the (U)PBE0 approximation $\langle S^2\rangle = 2.009$ was close to the exact value. Dispersion of the multi-electron spin in the equilibrium excited T_2, state [as calculated using the (RO)PBE0//(U)PBE0/cc-pVTZ method] was primarily distributed between oxygen (44%) and carbon (34%) atoms of the carbonyl group; the total contribution of the carbonyl group into the $DS = 1$ value was 78%.

The calculated dipole moment of the molecule decreased from 3.51 to 2.77 D upon the excitation of the T_2 triplet state. The Cope rearrangement of barbaralone in the T_2 state should occur easier than in the ground singlet state, as the corresponding energy barrier was decreased to $\Delta E_\cap$ 7.6 kcal/mol at the excitation.

Noteworthily, the study of excited states T_1 and T_2 involved minimization of the energy functional in the Bohr–Oppenheimer approximation without explicit accounting for the orthogonality of the wave functions with respect to each other and to the multi-electron wave function of the ground state. The mutual orthogonality of the full wave functions (functions of electrons and nuclei coordinates) was due to a significant difference between the equilibrium nuclei configurations, localization of vibrations at the different small space regions, and, consequently, the orthogonality of the vibration wave functions.

The idea of non-luminescent equilibrium (relaxed) excited states is equivalent to the idea of metastable isomers or conformers corresponding to the different minima of energy of a system of interacting atoms.

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