

Sigmatropic Hydrogen Shifts in Aryltetraphenylcyclopentadienes

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Abstract—Dynamic NMR has revealed intramolecular migrations of hydrogen atom over the periphery of the five-membered ring in 5-(*p*-tolyl)-1,2,3,4-tetraphenylcyclopentadiene in a deuterionitrobenzene solution with energy barrier $\Delta G_{180}^\ddagger = 24.8$ kcal/mol. Quantum-chemical DFT calculations B3LYP/6-311++G** have shown that such migrations in 1,2,3,4,5-pentaphenylcyclopentadiene in the gas phase occur in a chiral conformation of propeller type by the mechanism of 1,5-sigmatropic hydrogen shifts with retention of configuration through asymmetric transition state with energy barrier $\Delta E_{ZPE}^\ddagger = 25.9$ kcal/mol. Enantiomers **P** and **M** can readily interconvert into each other ($\Delta E_{ZPE}^\ddagger = 3.9$ kcal/mol) owing to synchronous flip rotations of the phenyl groups.

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Pentaarylcyclopentadienes and their metal complexes are wide-spread polydentate ligand systems; they behave as efficient asymmetric catalysts of cycloaddition reactions and other processes, high-performance luminophors, compounds with nonlinear optical properties, and prototypes of molecular rotor motors with conical gear transmission [1–3]. Therefore, it seems important to study the dynamic behavior of pentaarylcyclopentadienes related to their structural and stereochemical nonrigidity.

The prototropic tautomerism in cyclopentadiene ring and close in mechanism processes related to fast migrations of N, O, S, Se, Te-centered groups and halogens in this and akin cyclopropene and cycloheptatriene systems ($\Delta G^\ddagger = 6$ –25 kcal/mol) are described in the literature [4–13]. However, hydrogen migrations in pentaarylcyclopentadienes were not studied.

To reveal and study hydrogen shifts around the periphery of the five-membered carbon ring in pentaarylcyclopentadiene by dynamic ¹H NMR, we prepared 5-(*p*-tolyl)-1,2,3,4-tetraphenylcyclopentadiene **1** by the procedure [14] modified by us via reduction of 1,2,3,4-tetraphenyl-5-(*p*-tolyl)-cyclopentadien-5-ol **2** with LiAlH₄ in a benzene–ether mixture (Scheme 1).

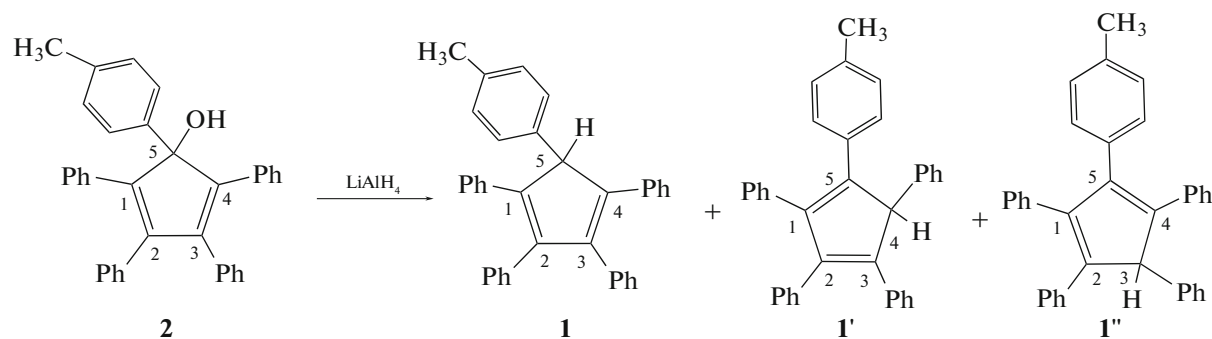
Compound **1** containing indicator methyl group in the *p*-tolyl moiety is formed in reaction course as an equilibrium mixture of isomers **1**, **1'**, and **1''** (0.2, 0.4, and 0.4, respectively). The ¹H NMR spectrum (300 MHz) of compound **1** in deuterionitrobenzene at ambient temperature displays three proton signals of the indicator methyl group at $\delta = 2.06$, 1.94, and 1.85 ppm with an intensity ratio of 1 : 2 : 2, which indicates equally probable location of hydrogen atom in all five positions of the cyclopentadiene ring, i.e., virtually equal energy state of isomers **1**, **1'**, and **1''**. A reversible broadening of signals of methyl protons independent of solution concentration is observed in the temperature range from +160 to +180°C. Such a spectral behavior is caused by the interconversion of isomers **1** \rightleftharpoons **1'** \rightleftharpoons **1''** due to intramolecular shifts of hydrogen atom over the periphery of the five-membered ring. The analysis of the temperature-dependent ¹H NMR spectra for compound **1** allowed us to assess the energy barrier of the process **1** \rightleftharpoons **1'** \rightleftharpoons **1''** in a deuterionitrobenzene solution: $\Delta G_{180}^\ddagger = 24.8$ kcal/mol, $k_{180} = 9.6$ s⁻¹.

To establish the mechanism of structural nonrigidity of compound **1**, whose activation parameters are at the upper boundary of the NMR time scale, which provides no possibility to detect coalescence of indicator signals and to study in detail this dynamic process, we performed theoretical modeling of possible routes of hydrogen migration around the periphery of the five-membered ring of 1,2,3,4,5-pentaphenylcyclopentadiene **3** using the B3LYP/6-311++G** DFT method [15].

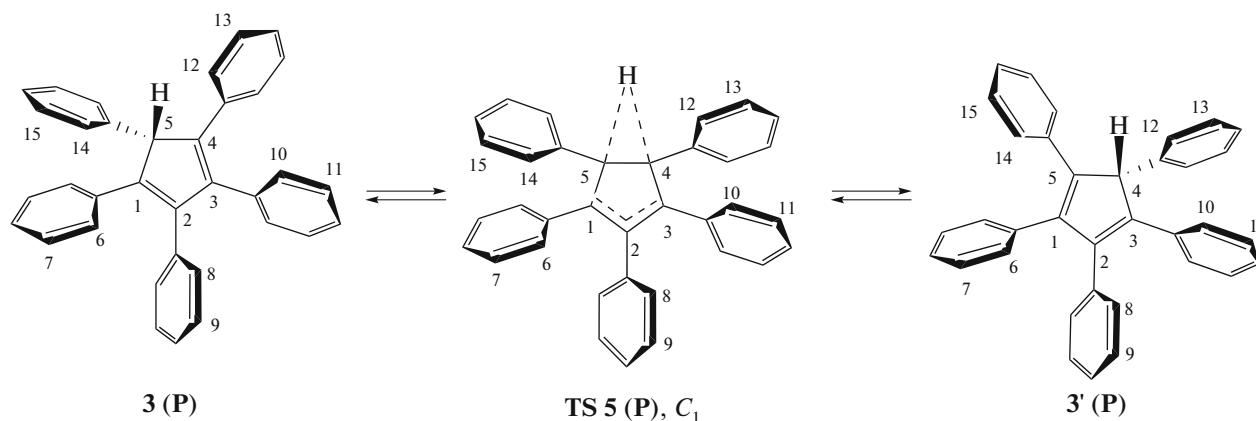
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Scheme 1.



Scheme 2.

According to the calculations for gas phase, structure **3** with a chiral conformation of propeller type of the $\text{Ph}_5\text{C}_5\text{H}$ molecule corresponds to the global minimum on the potential energy surface (PES) and is by 0.7 kcal/mol (ΔE_{ZPE}) more stable than structure **4** with

Total and relative energies for the structures of the ground states of pentaphenylcyclopentadiene conformers and energy barriers to hydrogen atom shifts therein in the gas phase calculated by the B3LYP/6-311++G(*d,p*) method^{a-c}

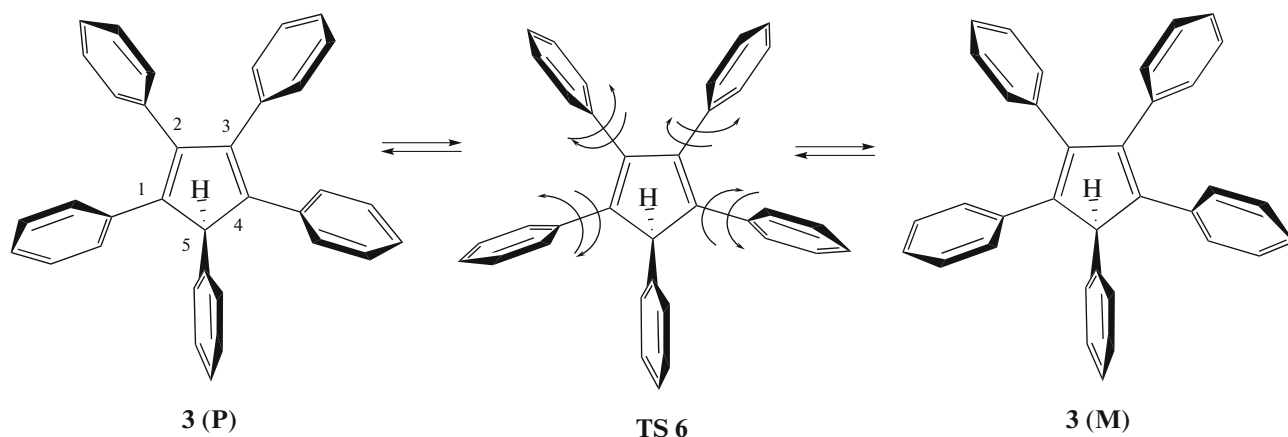
No. of structure	E_{total} , au	ΔE_{ZPE} , kcal/mol	ω_1 , cm^{-1}
3	-1349.70373	0	16
4	-1349.70231	0.7	12
TS 5	-1349.65814	25.9	-1220
TS 6	-1349.69731	3.9	-20
TS 7	-1349.65496	27.7	-1221

^a E_{total} is the total energy, 1 au = 627.5095 kcal/mol; ^b ΔE_{ZPE} is the relative energy corrected for the zero-point energy; ^c ω_1 , cm^{-1} , is the lowest value of harmonic vibrational frequency or the value of the sole imaginary harmonic vibrational frequency; ^c E_{ZPE} = -1349.20837 au (**3**).

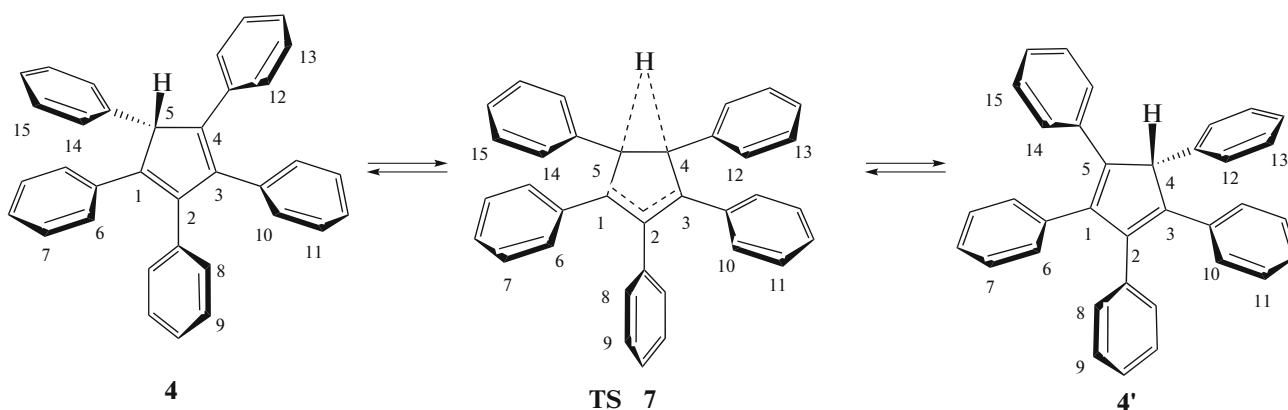
a non-propeller conformation (table, Schemes 2 and 4, Figs. 1 and 2). In structure **3 (P)** with a propeller conformation, four phenyl groups at the atoms C1–C4 of the cyclopentadiene ring are turned clockwise with respect to the plane of the five-membered ring with torsion angles $\text{C2C1C6C7} = 140.3^\circ$, $\text{C3C2C8C9} = 123.3^\circ$, $\text{C4C3C10C11} = 125.9^\circ$ and $\text{C5C4C12C13} = 122.8^\circ$, while the phenyl group at C5 is nearly perpendicular to the plane of the five-membered ring. In the corresponding enantiomer structure **3 (M)**, the phenyl groups at C1–C4 are turned counter-clockwise.

In conformer **4**, the molecule is close to a structure of C_s symmetry with the phenyl substituents at C1, C2 and C4, C3 turned to opposite sides relative to the plane of the five-membered ring (torsion angles $\text{C2C1C6C7} = 143.7^\circ$, $\text{C3C2C8C9} = 104.2^\circ$, $\text{C4C3C10C11} = 69.3^\circ$, and $\text{C5C4C12C13} = 35.1^\circ$). In the solid state, a structure similar to local minimum **4** is realized according to the data of X-ray diffraction study of $\text{Ph}_5\text{C}_5\text{H}$ [1], probably due to molecule packing effects in a crystal.

In structures **3** and **4**, 1,5- and 1,3-sigmatropic hydrogen shifts and hydrogen migration can occur via the formation of a tight ion pair; however, only transi-



Scheme 3.



Scheme 4.

tion states corresponding to 1,5 hydrogen shifts in agreement with the Woodward–Hoffmann rule were revealed on the PES.

1,5-Hydrogen shifts in conformer **3** proceed through transition state **TS 5** of symmetry C_1 with energy barrier $\Delta E_{\text{ZPE}}^\ddagger = 25.9$ kcal/mol, whose value agrees well with experimental data (Scheme 2, Fig. 1, table).

In asymmetric **TS 5 (P)** of propeller type, bond distances $C5-H$ and $C4-H$ are 1.325 and 1.307 Å, respectively. The bonds $C5C1$, $C1C2$, $C2C3$, $C3C4$ are leveled off (1.412–1.424 Å). The charge on hydrogen atom is positive and rather high (0.476e). All five phenyl substituents are turned clockwise (torsion angles $C1C5C14C15 = 134.1^\circ$, $C2C1C6C7 = 130.6^\circ$, $C3C2C8C9 = 121.3^\circ$, $C4C3C10C11 = 121.8^\circ$, $C5C4C12C13 = 127.1^\circ$). Propeller conformation (**P**) is retained at minima corresponding to **TS 5** (isomers **3** and **3'**).

Hydrogen atom can migrate in each of two enantiomers **3 (P)** or **3 (M)**. In its turn, enantiomers **3 (P)** and **3 (M)**, according to computational data, are read-

ily interconverted ($\Delta E_{\text{ZPE}}^\ddagger = 3.9$ kcal/mol) due to synchronous flip rotations, half-turns of the four phenyl groups at $C1-C4$ through **TS 6** of C_s symmetry (Scheme 3, table, Fig. 1), which leads to the fast racemization of this chiral ligand.

On the contrary, enantiomers **P** and **M** of pentaphenylcyclopentadiene metal complexes are rather stable. In particular, according to X-ray diffraction data, the crystal lattice of complex $[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})\{\text{C}(\text{=O})\text{H}\}\text{PMe}_3]$ contains two molecules where five phenyl groups are turned either clockwise or counter-clockwise [1].

The 1,5-hydrogen shifts in conformer **4** proceed via transition state **TS 7** of C_s symmetry with energy barrier $\Delta E_{\text{ZPE}}^\ddagger = 27.0$ kcal/mol (Scheme 4, Fig. 2, table), which is 1.1 kcal/mol higher than in conformer **3** through **TS 5**.

In **TS 7** of C_s symmetry, bond distances $C5-H$ and $C4-H$ are equal to 1.317 Å. Bond distances $C5C1$ and $C1C2$ ($C4C3$ and $C3C2$) are close to each other (1.421 and 1.413 Å). The charge on hydrogen atom is

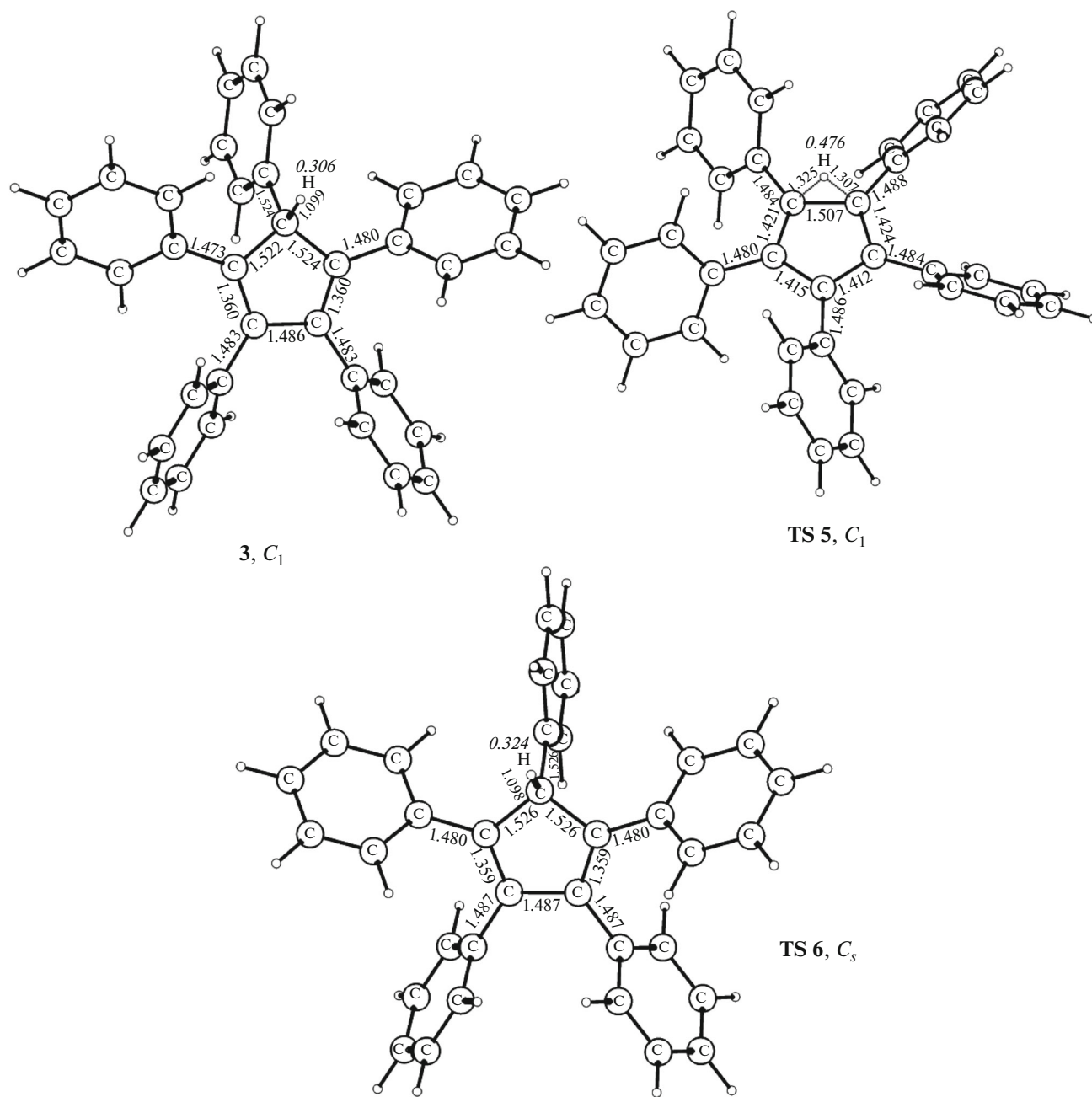


Fig. 1. Geometry parameters and charges (marked by italic) of main state structure of pentaphenylcyclopentadiene **3** (**P**) and transition states **TS 5** (**P**) and **TS 6**, respectively, for hydrogen atom migrations in **3** (**P**) and interconversions of enantiomers **3** (**P**) \rightleftharpoons **3** (**M**) in gas phase calculated by B3LYP/6-311++G(d,p) method. Bond distances in the figure are given in angstroms.

0.443e. Phenyl substituents at C5, C1 and C4, C3 in **TS 7** are turned to opposite sides (torsion angles C1C5C14C15 = 123.4°, C2C1C6C7 = 128.8°, C4C3C10C11 = 46.1°, C5C4C12C13 = 74.3°), while phenyl group at C2 is perpendicular to the plane of the five-membered ring.

Thus, the chiral conformation of propeller type **3** and the route of 1,5-sigmatropic hydrogen shifts through asymmetric transition state **3** \rightleftharpoons **TS 5** \rightleftharpoons **3'** are

energetically favorable for pentaphenylcyclopentadiene molecule in gas phase. The process of hydrogen migration includes synchronous turns of phenyl groups resulting in stable propeller conformation with retention of molecule chirality.

¹H NMR spectra were recorded on a Varian Unity spectrometer operating at 300 MHz.

5-(*p*-Tolyl)-1,2,3,4-tetraphenylcyclopentadiene **1**. Lithium aluminum hydride (0.15 g, 0.004 mol) was

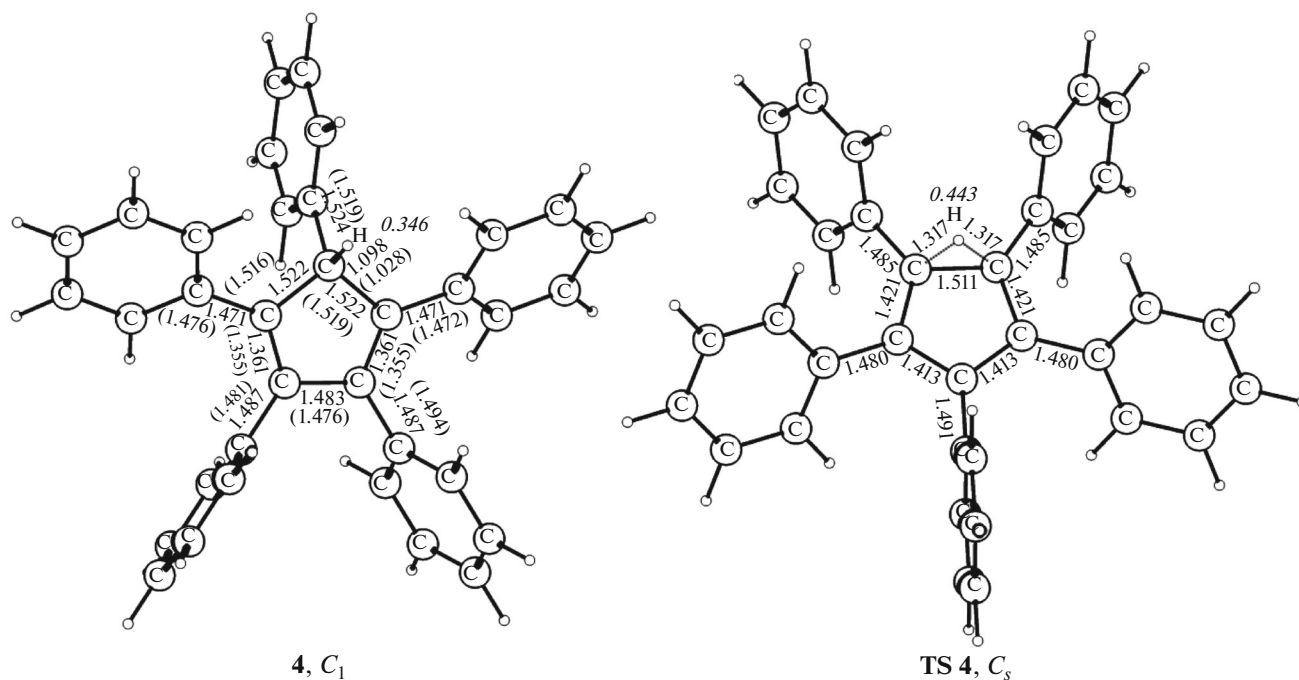


Fig. 2. Geometry parameters and charges (marked by italic) for the main state structure of pentaphenylcyclopentadiene **4** and transition state **TS 7** for hydrogen atom migrations in **4** in gas phase calculated by B3LYP/6-311++G(d, p) method. X-ray diffraction data are given parenthetically [1].

added to a solution of 0.95 g (0.002 mol) of compound **2** in 60 mL of a dry benzene–ether mixture (1 : 4). The mixture was heated under reflux on stirring for 12 h. The precipitate was separated by filtration. The solvent was removed in a vacuum. The residue was chromatographed on aluminum oxide using chloroform–hexane (1 : 3) as an eluent to give 0.57 g (62%) of compound **1** as colorless crystals, mp 156–159°C (155–160°C [14]). The data of the ^1H and ^{13}C NMR and IR spectra coincide with the literature data [14].

Quantum-chemical calculations were performed by the DFT method [15] using the B3LYP three-parameter potential with the 6-311++G(d,p) split-valence basis set in the gas phase with the use of the Gaussian-09 software package. All stationary points were identified by the calculation of the Hessian matrix. Charges on atoms were calculated by the Mulliken method.

ACKNOWLEDGMENTS

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