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Circumambulatory Rearrangements of 5-Halo-1,2,3,4,5-pentaphenylcyclopentadienes

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Abstract—DFT quantum chemical calculations at the CAM-B3LYP/Def2TZVP level of theory showed that intramolecular migrations of halogens in 5-halo-1,2,3,4,5-pentaphenylcyclopentadienes (C_5Ph_5Hlg, Hlg = F, Cl, Br, I) involve chiral conformation of their molecules with a propeller arrangement of phenyl groups via 1,5-sigmatropic shifts around the five-membered ring through asymmetric transition states with energy barriers $\Delta E^{\ne}_{\mathrm{ZPE}}$ of 42.5 (F), 26.2 (Cl), 20.2 (Br), and 15.2 kcal/mol (I). The results were consistent with the data of dynamic NMR spectroscopy. The *P* and *M* enantiomers are readily interconvertible ($\Delta E^{\ne}_{\mathrm{ZPE}}$ = 1.7–3.7 kcal/mol) by way of synchronous flips of the phenyl groups. The calculated barriers to alternative 1,3-halogen shifts in C_5Ph_5Hlg are considerably higher than those for 1,5-shifts: $\Delta E^{\ne}_{\mathrm{ZPE}}$ = 60.7 (F), 38.6 (Cl), 32.0 (Br), and 27.9 kcal/mol (I).

Keywords: halopentaphenylcyclopentadienes, circumambulatory rearrangement, molecular propellers, chirality, DFT calculations

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Structure determination and study of structural nonrigidity of pentaarylcyclopentadienyl halides are of great importance since these compounds are precursors to a wide range of cyclopentadiene derivatives with practically useful properties, including complexes that are prototypes of molecular motors [1–5]. In addition, numerous metal complexes with pentaarylcyclopentadienyl ligands are widely used to catalyze asymmetric cycloadditions and a number of other important reactions [1, 6] and are highly efficient luminophores and compounds with nonlinear optical properties [7–9]. Pentaphenylcyclopentadiene itself is a fluorescent molecular rotor whose emission is induced by intra- and intermolecular interactions between phenyl rings [10].

By using ^1H and ^{13}C NMR techniques we previously revealed and studied intramolecular migrations of halogens in halocyclopentadiene derivatives. It was found that chlorine and bromine atoms migrate around the five-membered ring of tolyltetraphenylcyclopentadiene with energy barriers $\Delta G^{\ne}_{298}$ of 25.9 and 18.1 kcal/mol, respectively [11–13]. The migrations of chlorine and bromine around pentamethyl cyclopentadienepentacarboxylate and tetramethyl alkylcyclopentadienetetracarboxylates were characterized by barriers of 25.7–27.3 and 16.2–22.9 kcal/mol, respectively [14]. Circumambulatory rearrangements of 5-iodocyclopentadiene are much faster, and the corresponding energy barrier is 14 kcal/mol [15]. According to DFT calculations, 5-iodocyclopentadiene in a rotating electric field behaves as a molecular rotor in which the iodine atom rapidly moves in one direction around the five-membered ring (k_{298} = 630 s^{-1}) [16].

Rearrangements involving halogen migration in cyclopolyenes and other systems, in addition to sigmatropic shifts of hydrogen and some other organic, organoelement, and organometallic groups, are widely used in organic and organometallic chemistry [12, 13, 17–21].

In this work we examined possible halogen migration paths in 5-halo-1,2,3,4,5-pentaphenylcyclopentadienes **1a**–**1d** [Hlg = F (**a**), Cl (**b**), Br (**c**), I (**d**)] and structures of the corresponding transition states by DFT quantum chemical calculations at the CAM-B3LYP/Def2TZVP level of theory. The available experimental data do not allow appropriate selection of one of the alternative paths for fluctuating behavior of compounds **1a**–**1d**. Halogen migration around the cyclopentadiene ring of **1a**–**1d** can be mediated by 1,5- or 1,3-sigmatropic shifts, as well as by randomization through the formation of tight ion pairs. Furthermore,

Table 1. Calculated (CAM-B3LYP/Def2TZVP) total and relative energies of the ground states of 5-halo-1,2,3,4,5-pentaphenylcyclopentadienes **1a**–**1d** and transition states for halogen migration therein in the gas phase[a–c]

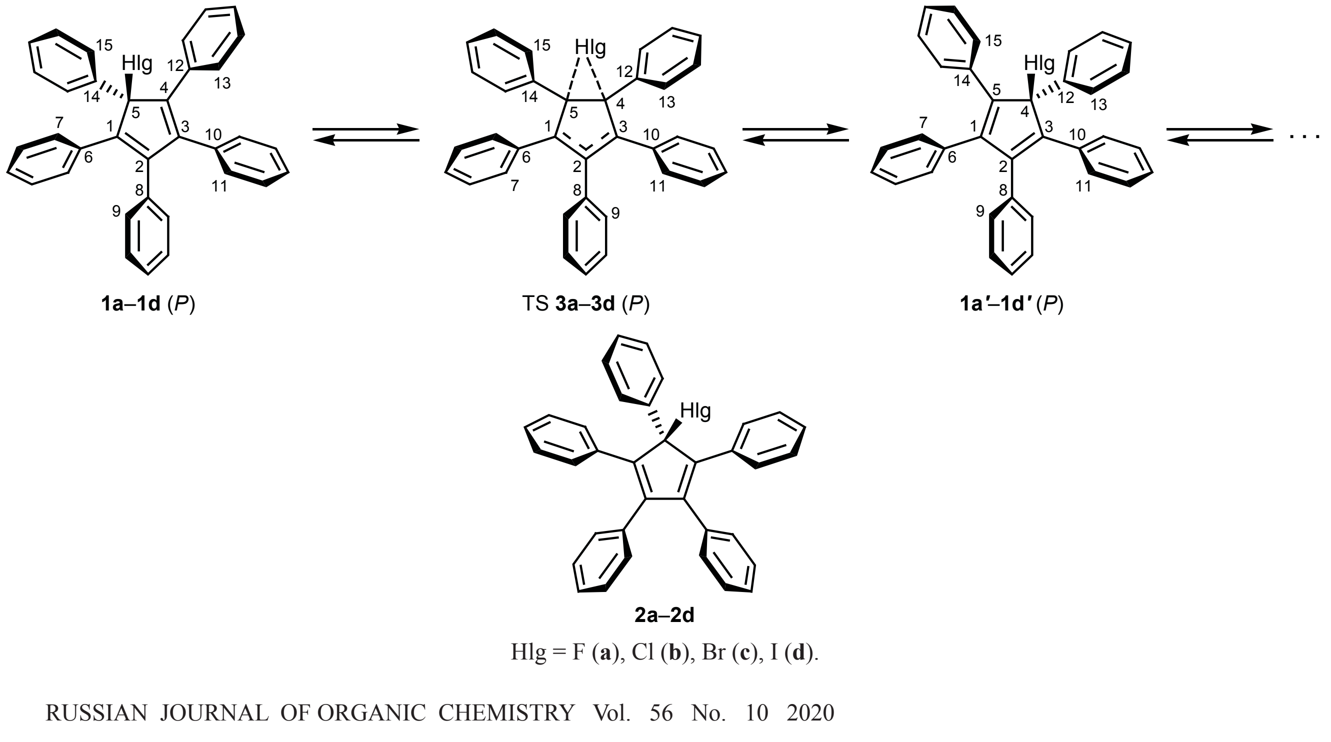
Comp. no.	E_{tot}, a.u.	ΔE_{ZPE}, kcal/mol	ω_1, cm^{-1}
1a	–1448.32371	0	19
TS **3a**	–1448.25329	42.5	–717
TS **4a**	–1448.22319	60.7	–347
TS **5a**	–1448.31759	3.7	–24
TS **6a**	–1448.24807	45.3	–752
1b	–1808.68406	0	14
TS **3b**	–1808.64051	26.2	–468
TS **4b**	–1808.62001	38.6	–196
TS **5b**	–1808.68008	2.4	–23
1c	–3922.73668	0	16
TS **3c**	–3922.70280	20.2	–379
TS **4c**	–3922.68332	32.0	–179
TS **5c**	–3922.73303	2.1	–24
1c (solvent C_6H_5Cl)	–3922.74403	0	16
TS **3c** (solvent C_6H_5Cl)	–3922.71131	19.5	–296
1d	–1646.16402	0	19
TS **3d**	–1646.13832	15.2	–329
TS **4d**	–1646.11743	27.9	–232
TS **5d**	–1646.16084	1.7	–25

[a] E_{tot} is the total energy, 1 a.u. = 627.5095 kcal/mol.

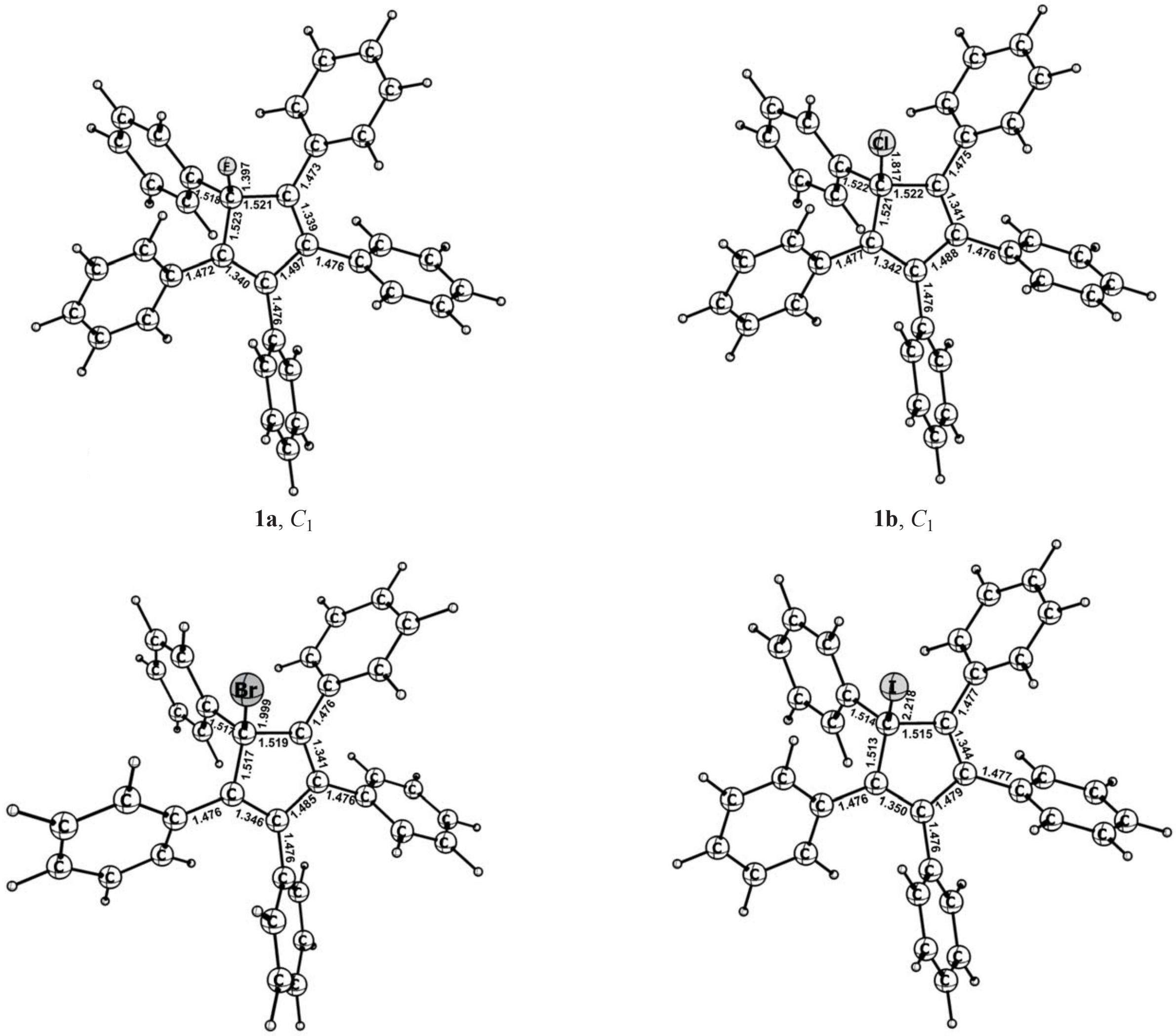
[b] ΔE_{ZPE} is the relative energy corrected for zero-point vibrational energy; ω_1 is the least or single imaginary harmonic vibration frequency.

[c] E_{ZPE} = –1447.82915 (**1a**), –1808.19108 (**1b**), –3922.24429 (**1c**), –3922.25176 (**1c** + C_6H_5Cl), –1645.67205 a.u. (**1d**).

Scheme 1.



Hlg = F (**a**), Cl (**b**), Br (**c**), I (**d**).



1a, C_1 **1b**, C_1

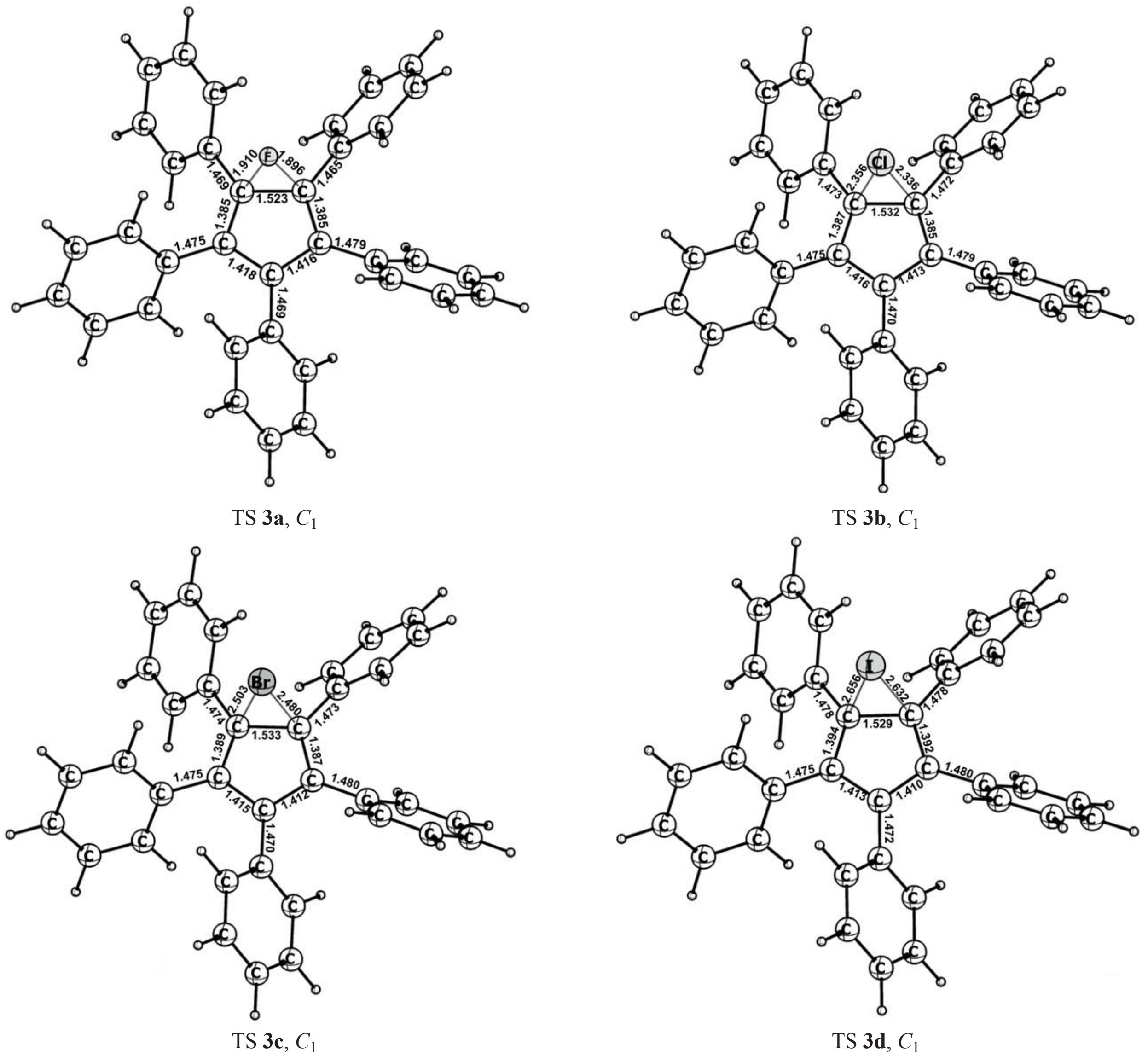
1c, C_1 **1d**, C_1

Fig. 1. Calculated (CAM-B3LYP/Def2TZVP) geometric parameters of chiral structures of compounds **1a**–**1d** (*P*) in the ground state in the gas phase. Hereinafter, the bond lengths are given in Å.

there are no published data on the effects of all halogens on the activation barrier and mode of their migration in the pentaphenylcyclopentadiene system, nor conformations of these compounds in the ground and transition states were studied. In order to elucidate these problems, migration of halogens around the five-membered ring of pentaphenylcyclopentadiene was simulated by quantum chemical calculations, and the calculated activation barriers for these processes were compared with available experimental data.

The calculations showed that structures of **1a**–**1d** corresponding to minima on the potential energy surfaces for the gas phase have chiral propeller [22] conformation (Table 1, Scheme 1, Fig. 1). Alternative structures **2a**–**2d** where the phenyl groups are oriented in a nonpropeller fashion and are turned to different sides with respect to the five-membered ring plane were not localized on the PESs.

The four phenyl groups on C^1–C^4 of the cyclopentadiene ring of chiral propeller structures **1a**–**1d** (*P*) are turned clockwise with respect to the five-membered ring through the following dihedral angles: $C^2C^1C^6C^7$ 137.3° (**1a**), 131.3° (**1b**), 141.8° (**1c**), 149.9° (**1d**); $C^3C^2C^8C^9$ 125.7° (**1a**), 128.6° (**1b**), 126.9° (**1c**), 125.4° (**1d**); $C^4C^3C^{10}C^{11}$ 127.0° (**1a**), 126.6° (**1b**), 126.0° (**1c**), 124.2° (**1d**); and $C^5C^4C^{12}C^{13}$ 123.6° (**1a**), 119.9° (**1b**), 115.8° (**1c**), 117.0° (**1d**). The phenyl group on C^5 is almost orthogonal to the cyclopentadiene ring plane. The benzene rings on C^1–C^4 of the corresponding *M* enantiomers of **1a**–**1d** are turned counterclockwise.



TS **3a**, C_1 TS **3b**, C_1

TS **3c**, C_1 TS **3d**, C_1

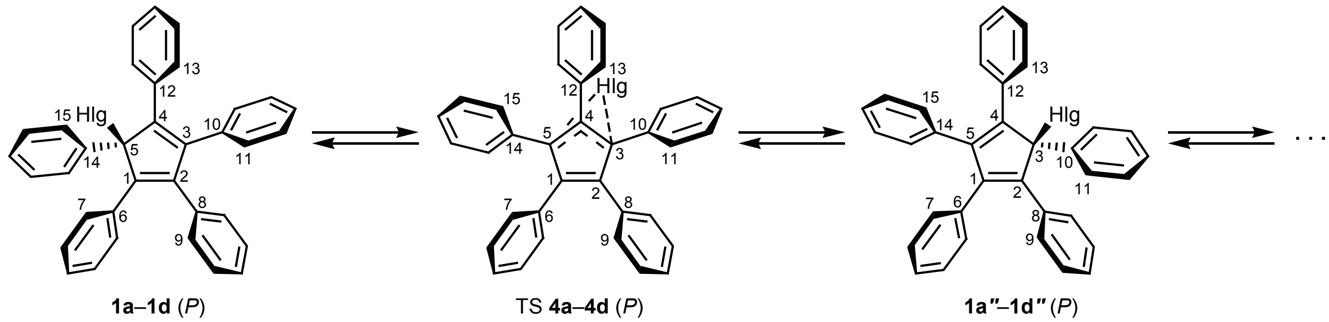
Fig. 2. Calculated (CAM-B3LYP/Def2TZVP) geometric parameters of chiral structures of transition states **3a**–**3d** (*P*) for 1,5-halogen shift in the gas phase.

The C^5–Hlg bond lengths in **1a**–**1d** are C^5–F 1.397, C^5–Cl 1.817, C^5–Br 1.999, and C^5–I 2.218 Å. The charge on the halogen atom in the most favorable structures **1a**–**1d** changes from negative on the fluorine atom to positive on the iodine atom: –0.357 (F), –0.043 (Cl), 0.011 (Br), 0.111 *e* (I).

Transition states (TS) **3a**–**3d** and **4a**–**4d** with C_1 symmetry, which correspond to sigmatropic 1,5- and 1,3-halogen shifts around the five-membered ring, were localized on the PESs for halocyclopentadienes **1a**–**1d** (Table 1; Schemes 1, 2; Figs. 2, 3). No structures corresponding to the randomization mechanism involving tight ion pairs were identified, which indicated that this mechanism is not operative in the migration of halogens around the five-membered ring of halopentaphenylcyclopentadienes **1a**–**1d**.

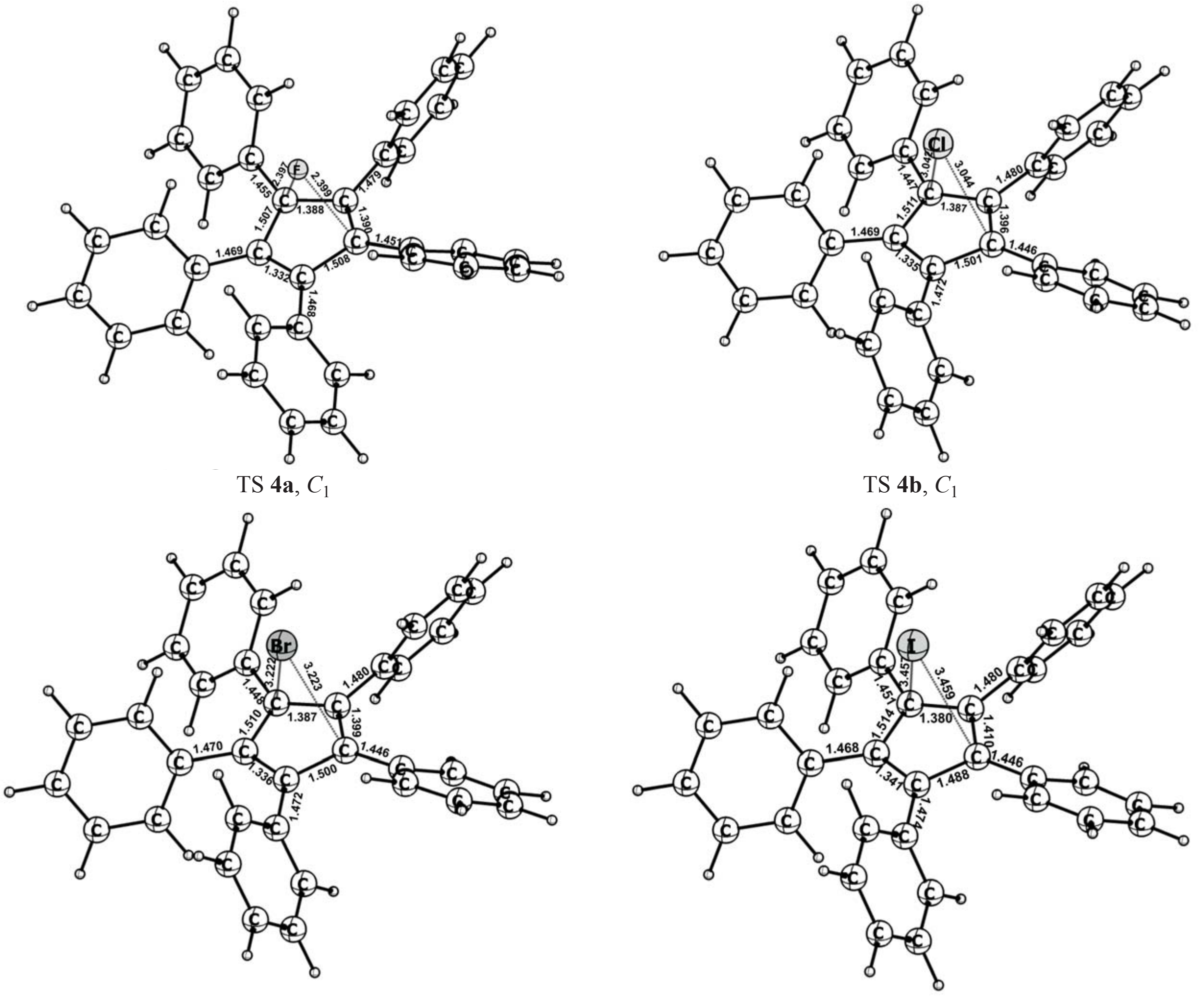
The distances between the migrating halogen atom and two nearest carbon atoms of the cyclopentadiene ring in asymmetric propeller-like transition states **3a**–**3d** (*P*) for 1,5-shifts (Scheme 1, Fig. 2) increase in going from fluorine to iodine: 1.896 and 1.910 (F), 2.335 and 2.356 (Cl), 2.480 and 2.503 (Br), and 2.632 and 2.655 Å (I). The cyclopentadiene ring in TS **3a**–**3d** is planar, and the π-electron density is delocalized over the entire ring, as follows from similarity of the C^5–C^1, C^1–C^2, C^2–C^3, and C^3–C^4 bond lengths. All five benzene rings are turned clockwise with respect to the five-membered ring; the torsion angles are $C^1C^5C^{14}C^{15}$

Scheme 2.



Hlg = F (**a**), Cl (**b**), Br (**c**), I (**d**).

143.1° (**1a**), 150.7° (**1b**), 151.9° (**1c**), 153.6° (**1d**); $C^2C^1C^6C^7$ 125.6° (**1a**), 126.9° (**1b**), 128.2° (**1c**), 130.4° (**1d**); $C^3C^2C^8C^9$ 129.8° (**1a**), 128.4° (**1b**), 127.4° (**1c**), 126.2° (**1d**); $C^4C^3C^{10}C^{11}$ 115.8° (**1a**), 113.5° (**1b**), 112.5° (**1c**), 113.2° (**1d**); $C^5C^4C^{12}C^{13}$ 132.0° (**1a**), 135.9° (**1b**), 137.7° (**1c**), 139.1° (**1d**). The energy minima on the PESs corresponding to 1,5-halogen shift through TS **3a**–**3d** (*P*), i.e., isomeric structures **1a**–**1d** and **1a′**–**1d′**, retain propeller conformation of the phenyl rings (*P*).

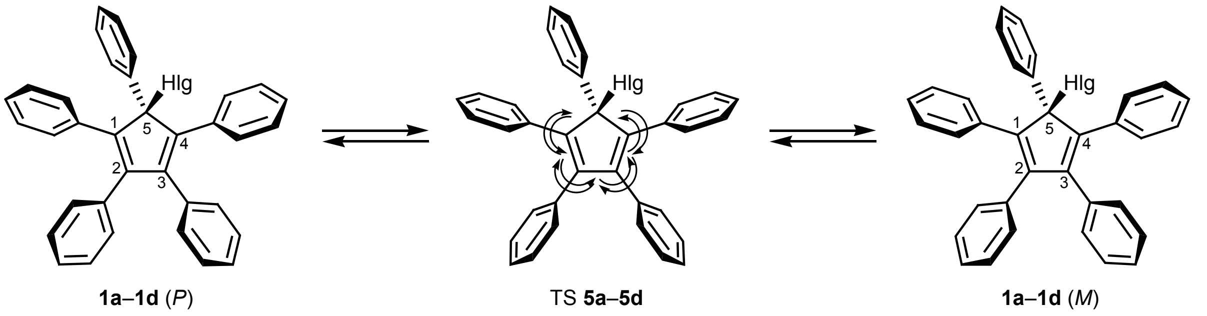


TS **4a**, C_1 TS **4b**, C_1

TS **4c**, C_1 TS **4d**, C_1

Fig. 3. Calculated (CAM-B3LYP/Def2TZVP) geometric parameters of chiral structures of transition states **4a**–**4d** (*P*) for 1,3-halogen shift in the gas phase.

Scheme 3.



Hlg = F (**a**), Cl (**b**), Br (**c**), I (**d**).

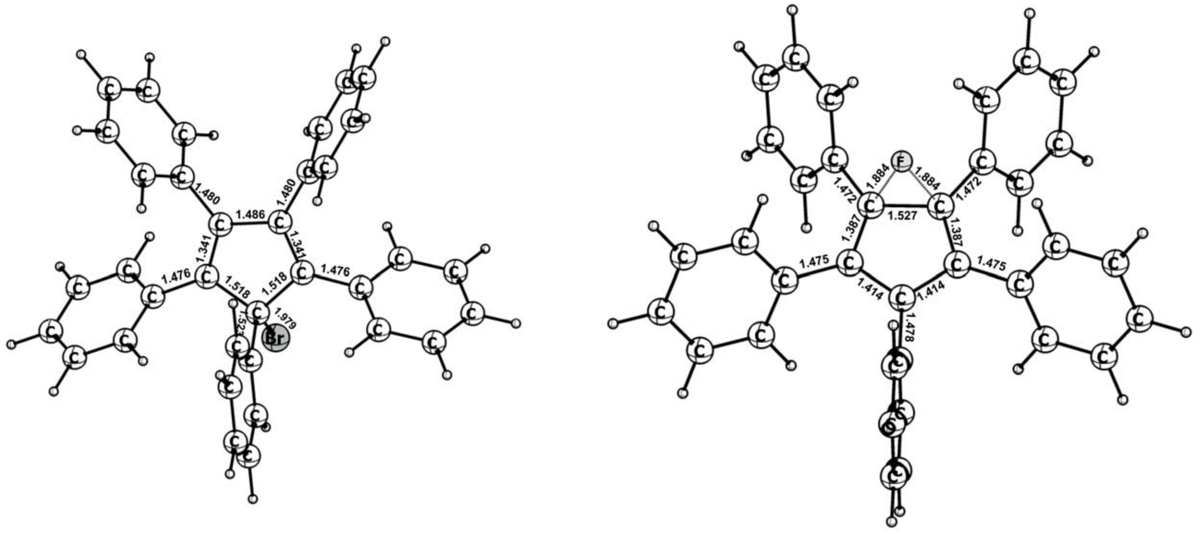
The calculated charges on the halogen atom in TS **3a**–**3d** are negative and are fairly large for fluorine, chlorine, and bromine atoms [–0.514 (F), –0.301 (Cl), –0.221 (Br), –0.063 (I)], which suggests considerable charge separation between the migrating atom and the rest of the system. The energy barriers to 1,5-halogen shifts around the five-membered ring of **1a**–**1d** through TS **3a**–**3d** were estimated at $\Delta E^{\neq}_{\mathrm{ZPE}}$ = 42.5 (F), 26.2 (Cl), 20.2 (Br), and 15.2 kcal/mol (I) (Table 1).

The rearrangement of **1c** was also simulated with inclusion of solvent effect using the PCM model. It was shown that the barrier to 1,5-shift of bromine in chlorobenzene is lower by 0.7 kcal/mol than in the gas phase and is $\Delta E^{\neq}_{\mathrm{ZPE}}$ = 19.5 kcal/mol. This value is very consistent with the barrier to bromine migration in **1c** determined experimentally by dynamic NMR spectroscopy [11].

Halogen atoms are capable of migrating in each of the two enantiomers **1a**–**1d** (*P*) and **1a**–**1d** (*M*). According to the calculations, these enantiomers are readily interconvertible with energy barriers $\Delta E^{\neq}_{\mathrm{ZPE}}$ of 3.7 (F), 2.4 (Cl), 2.1 (Br), and 1.7 kcal/mol (I) via synchronous flips [22] (half-turns) of four phenyl substituents on C^1–C^4 through TS **5a**–**5d** with C_s symmetry (Scheme 3, Fig. 4, Table 1). This leads to fast racemization of **1a**–**1d**.

It should be noted that, unlike structures **1a**–**1d**, the *P* and *M* enantiomers of pentaphenylcyclopentadienyl metal complexes are stable. According to the X-ray diffraction data, a unit cell of the complex $[Fe(\eta^5\text{–}C_5Ph_5)(CO)\{C(=O)H\}PMe_3]$ contains two molecules in which five phenyl groups are turned either clockwise or counterclockwise [1].

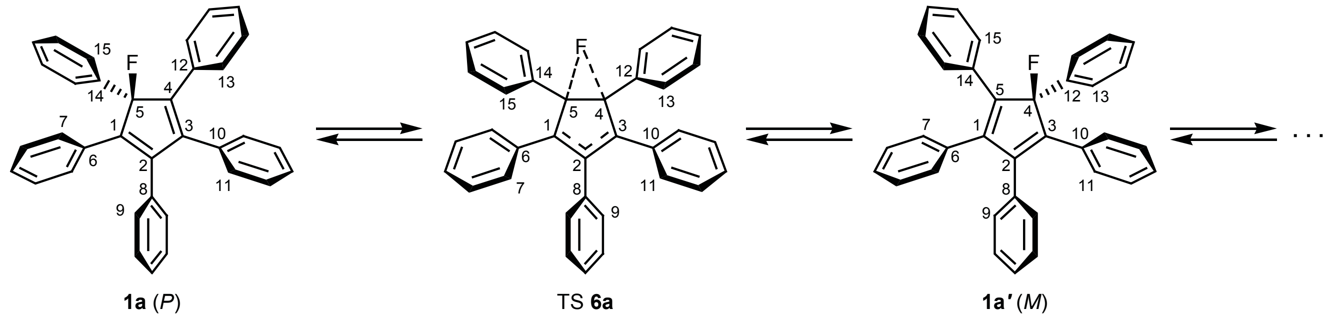
A competing mechanism of sigmatropic 1,5-fluorine shift through TS **6a** with C_s symmetry was revealed for compound **1a**. Its energy barrier $\Delta E^{\neq}_{\mathrm{ZPE}}$ = 45.3 kcal/mol (Scheme 4, Fig. 4, Table 1) is higher by 2.8 kcal/mol than that for TS **3a**, which suggests higher probability



TS **5c**, C_s TS **6a**, C_s

Fig. 4. Calculated (CAM-B3LYP/Def2TZVP) geometric parameters of transition state **5c** for the interconversion of the *P* and *M* enantiomers of **1c** and transition state **6a** (C_s symmetry) for 1,5-shift of fluorine in the gas phase.

Scheme 4.



of the path involving chiral TS **3a**. The C^5–F and C^4–F distances in TS **6a** are equal to each other (1.884 Å). The C^5–C^1 and C^1–C^2 (C^4–C^3 and C^3–C^2) bond lengths are also very similar (1.387 and 1.414 Å). The benzene rings on C^5, C^1 and C^4, C^3 in TS **6a** are turned in opposite directions (torsion angles C^{1}C^{5}C^{14}C^{15} 131.1°, C^{2}C^{1}C^{6}C^7 125.1°, C^{4}C^{3}C^{10}C^{11} 47.3°, C^{5}C^{4}C^{12}C^{13} 67.7°), and the benzene ring on C^2 is orthogonal to the five-membered ring plane.

The migrating halogen atom in transition states TS **4a**–**4d** (Scheme 3, Fig. 3) for 1,3-sigmatropic shifts is more distant from the cyclopentadiene ring than in TS **3a**–**3d**; the distances between the halogen atom and two nearest cyclopentadiene carbon atoms are 2.397 and 2.399 (F), 3.042 and 3.044 (Cl), 3.222 and 3.224 (Br), and 3.457 and 3.459 Å (I). The C^4 atom in TS **4a** (Hlg = F) deviates from the plane formed by the four other ring atoms so that the torsion angle C^{1}C^{2}C^{3}C^4 is –8.3°. The cyclopentadiene ring in TS **4b**–**4d** (Hlg = Cl, Br, I) is almost planar. The π-electron density in TS **4a**–**4d** is delocalized over the C^{5}C^{4}C^3 fragment, as follows from similar lengths of the C^5–C^4 and C^4–C^3 bonds, while the C^1–C^2 bond is double. Charge separation between the halogen atom and pentaphenylcyclopentadiene system in TS **4a**–**4d** is significantly greater than in TS **3a**–**3d**: all halogen atoms possess a large negative charge, –0.720 (F), –0.719 (Cl), –0.691 (Br), and –0.621 *e* (I)].

The calculated energy barriers to 1,3-halogen shift in compounds **1a**–**1d** through TS **4a**–**4d** are significantly higher than those to 1,5-shift through TS **3a**–**3d** and are $\Delta E^{\ddagger}_{\mathrm{ZPE}}$ = 60.7 (F), 38.6 (Cl), 32.0 (Br), and 27.9 kcal/mol (I) (Table 1). The differences between the barriers to 1,5- and 1,3-halogen shifts in **1a**–**1d** are fairly large, $\Delta\Delta E^{\ddagger}_{\mathrm{ZPE}}$ = 18.2 (F), 12.4 (Cl), 11.8 (Br), and 12.7 kcal/mol (I). Therefore, the circumambulatory rearrangements of 5-halo-1,2,3,4,5-pentaphenylcyclopentadienes **1a**–**1d** should proceed via sigmatropic 1,5-halogen shifts around the five-membered ring in keeping with the Woodward–Hofmann orbital symmetry conservation rules. The results of calculations are in good agreement with the barriers to migration of chlorine and bromine in pentaphenyl- and tolyltetraphenylcyclopentadiene systems, determined experimentally by dynamic NMR spectroscopy [11].

Our calculations revealed peculiar features of halogen migration paths around the five-membered ring of pentaphenylcyclopentadiene. In particular, energetic preference of chiral propeller conformations of molecules **1a**–**1d** in the ground state and sigmatropic 1,5-halogen shifts through asymmetric transition states [**1a**–**1d** ⇄ TS **3a**–**3d** ⇄ **1a′**–**1d′** ⇄ …] have been established. The halogen migration processes involve synchronous rotations of the phenyl groups, leading to stable propeller conformations with the same helical chirality. Likewise, as we have recently shown by DFT calculations, sigmatropic 1,5-hydrogen shifts in 1,2,3,4,5-pentaphenylcyclopentadiene also involve propeller conformation and asymmetric transition state [23]. The experimental and theoretical energy barriers to halogen migration in the pentamethyl cyclopentadienepentacarboxylate and unsubstituted cyclopentadiene systems [14, 16, 24] are similar to those found for halopentaphenylcyclopentadienes.

It should be noted that, according to theoretical calculations, sigmatropic 1,5-shifts of chlorine and bromine in (*Z*,*Z*)-penta-1,3-dienes should be suprafacial, whereas antarafacial pathway is energetically more favorable for 1,5-sigmatropic migration of fluorine [25]. Halogen migration in related cyclopropene and cycloheptatriene derivatives, whose ionization is favored by the formation of stable aromatic cations, may follow both ionization–recombination mechanism through tight ion pairs and sigmatropic shifts, depending on the solvent polarity [12, 26, 27].

EXPERIMENTAL

Quantum chemical calculations were performed using CAM-B3LYP functional and Def2TZVP basis set included in Gaussian 09 software package both for the gas phase and with account taken of solvent effect in terms of the polarizable continuum model (PCM). Stationary points on the potential energy surfaces were identified by calculating the corresponding Hessian matrices. The charges on atoms were calculated by the natural bond orbital (NBO) method.

CONCLUSIONS

In summary, DFT CAM-B3LYP/Def2TZVP calculations have shown that halogen migration around the five-membered ring of 5-halo-1,2,3,4,5-pentaphenylcyclopentadienes occurs via 1,5-sigmatropic shifts in chiral propeller conformers through asymmetric transition states; the *P* and *M* enantiomers are readily interconvertible by way of synchronous flips of phenyl substituents. Energetic preference of 1,5-halogen shift around the five-membered ring in comparison to 1,3-shift has been revealed. The migrating ability of halogens increases in the series F < Cl < Br < I in parallel with their atomic radii.

Fast 1,5-shifts of chlorine, bromine, and iodine around the five-membered ring of pentaphenylcyclopentadiene give rise to five degenerate isomers; however, similar processes in unsymmetrical pentaarylcyclopentadienyl halides could lead to isomer mixtures, which should be taken into account while planning syntheses with the use of such reagents.

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CONFLICT OF INTEREST

The authors declare the absence of conflict of interest.

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