Physical Chemistry

Corannulene derivatives as models for calculations of fullerene derivatives

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Hypothetical derivatives of corannulene $C_{20}H_{10}$ (Cor), namely, $CorX_5{}^{\cdot}$ radicals, $CorX_5{}^-$ anions (X = H, Cl, or Br), and their η^5-π-complexes with SiCp, were calculated by the MNDO/PM3 method. The possibilities of using the results of these calculations for modeling the electronic structure and geometry of fragments of the analogous complexes of the fullerene derivatives $C_{60}X_5$ are discussed. Calculations of $C_{60}X_5{}^{\cdot}$ radicals and $C_{60}X_5{}^-$ anions were also carried out. In all the compounds under study, the X atoms are attached to carbon atoms in α positions with respect to the same five-membered ring.

Key words: corannulene, fullerene, π-complexes, radicals, MNDO/PM3 method.

It is known that the polyhedral carbon cluster C_{60} (**1**), which is the most extensively studied representative of the fullerene family, consists of 12 five-membered rings and 20 six-membered rings. The cluster contains 60 π-electrons and two types of C—C bonds with bond lengths of 1.39 and 1.45 Å. The fullerene polyhedron can formally provide a different number of π-electrons to form η^n-complexes (n = 1 — 6) with various ligands. One of the characteristic features of C_{60} fullerene is its ability to add free radicals to one or more carbon atoms.[1] Various η^2-derivatives of C_{60} and C_{70} fullerenes with transition metals have been synthesized and studied (see Refs. 1 and 2 and references therein). However, all attempts to prepare η^n-complexes of fullerene with $n \geq 3$, which are stable under normal conditions, have failed.

The problem of the existence of η^5- and η^6-complexes of C_{60} fullerene has been discussed in a series of theoretical works.[3—5] Quantum-chemical calculations demonstrated[5] that if η^5-π-complexes of fullerene with MCp^+ moieties (where M is a transition-metal atom) occur, they should be less stable than the analogous classical $M(Cp)_2$ sandwich systems. It was established[5] that one of the causes of the decrease in the stability of the system that is formed as a result of replacement of one Cp ligand in $M(Cp)_2$ by C_{60} is the fact that there is a higher degree of delocalization of π-electrons in the C_{60} molecule than in the cyclopentadienyl anion. This leads to a sharp decrease in the contributions of the frontier MOs to the π-electron density on the atoms of the corresponding five-membered ring. However, it was found[6] that attachment of hydrogen atoms to all carbon atoms of C_{60} adjacent to the same five-membered ring substantially increases the ability of this polyhedral moiety to form η^5-π-complexes.

Fullerenes C_n with $n \geq 60$ contain no less than 360 electrons. Because of this, it is difficult to study these

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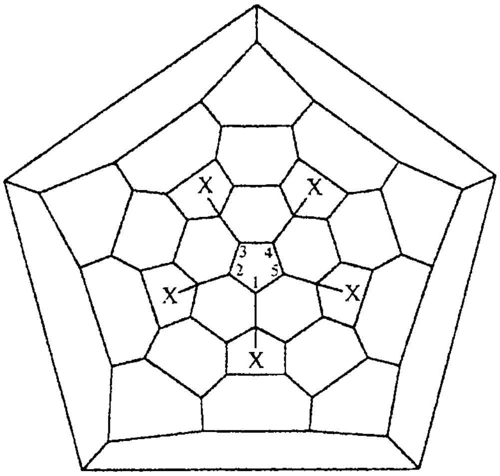

Fig. 1. Schlegel diagrams of C_{60} fullerene (**1**), $C_{60}X_5^{\cdot}$ radicals (**1a**—**c**), and $C_{60}X_5^-$ anions (**3a**—**c**). X = H (**a**), Cl (**b**), and Br (**c**).

systems by high-level quantum-chemical methods. In this connection, it is of particular interest to search for molecules with a substantially smaller number of electrons that can be used for modeling certain properties of polyhedral carbon clusters with a rather large number of atoms. Corannulene (Cor) (**2**), which was synthesized in 1966,[7] is the simplest system whose carbon framework is close to that of the polycyclic bowl-shaped C_{60} fragment. However, the conjugated system of corannulene is substantially less extended than that of fullerene. Therefore, corannulene as well as analogous bowl-shaped compounds with a large number of atoms that have been synthesized recently[8,9] are convenient systems for theoretical studies of the factors favorable to the formation of various derivatives of C_{60} fullerene.[10] In addition, these systems can help elucidate the effect of spherical conjugation on their reactivities.

In this work, we discuss the use of the corannulene molecule and its $CorX_5$ derivatives in which X atoms are attached to carbon atoms adjacent to the central pentagon for modeling the molecular and electronic structures of η^5-π-complexes of C_{60} fullerene and its $C_{60}X_5$ derivatives with the SiCp moiety. The molecular and electronic structures of the following compounds were studied: C_{60} (**1**), $C_{60}X_5^{\cdot}$ (**1a**—**c**), $C_{60}X_5^-$ and (**3a**—**c**) (Fig. 1); $C_{20}H_{10}$ (Cor) (**2**), $CorX_5^{\cdot}$ (**2a**—**c**), and $CorX_5^-$ (**4a**—**c**) (Fig. 2); $C_{60}X_5SiCp$ (**5a**—**c**) (Fig. 3); and $CorX_5SiCp$ (**6a**—**c**) (Fig. 4).

Calculations were carried out by the MNDO/PM3 method[11] using the GAMESS program.[12] The RHF (for systems with even numbers of electrons) and ROHF (for radicals) approximations were used.

Results and Discussion

The energies of the above-mentioned compounds were optimized for all geometric parameters taking into

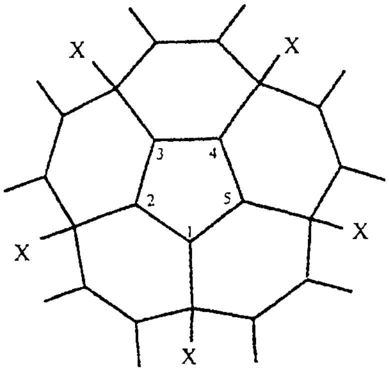

Fig. 2. Schlegel diagrams of $C_{20}H_{10}$ corannulene (Cor) (**2**), $CorX_5^{\cdot}$ radicals (**2a**—**c**), and $CorX_5^-$ anions (**4a**—**c**). X = H (**a**), Cl (**b**), and Br (**c**).

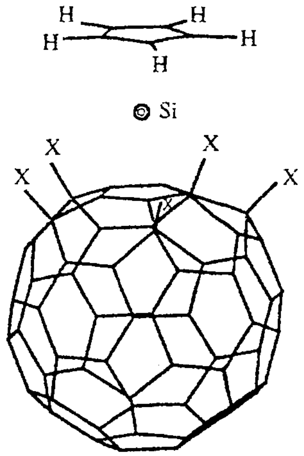

Fig. 3. Structures of the sandwich complexes of the fullerene derivatives $C_{60}X_5SiCp$ (**5a**—**c**). X = H (**a**), Cl (**b**), and Br (**c**).

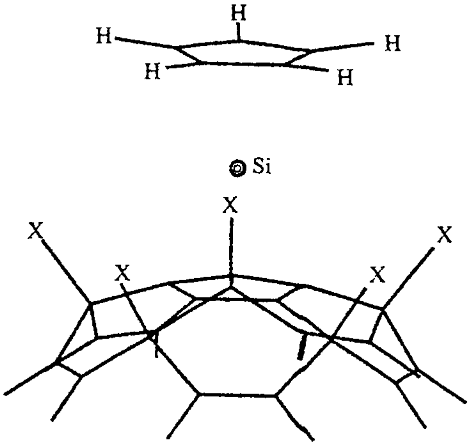

Fig. 4. Structures of the sandwich complexes of the corannulene derivatives $CorX_5SiCp$ (**6a**—**c**). X = H (**a**), Cl (**b**), and Br (**c**).

Table 1. Heats of formation (ΔH_f^0) of radicals **1a—c** and **2a—c**, energies of the highest occupied (E_{HOMO}) and lowest unoccupied (E_{LUMO}) levels, charges q_i on the carbon atoms of the pentagon under consideration, and total charges Q (Σq_i) on the pentagon calculated by the MNDO/PM3 method

Particle	ΔH_f^0	Charge/au				Energy/eV	
		q_1	$-q_2, -q_5$	$-q_3, -q_4$	$-Q$	$-E_{HOMO}$	$-E_{LUMO}$
$C_{60}H_5^{\cdot}$ (**1a**)	723.6	0.02	0.15	0.05	0.38	6.09	2.36
$C_{60}Cl_5^{\cdot}$ (**1b**)	716.5	0.05	0.14	0.04	0.31	6.76	2.74
$C_{60}Br_5^{\cdot}$ (**1c**)	767.0	0.06	0.11	0.02	0.20	6.78	2.80
$CorH_5^{\cdot}$ (**2a**)	151.4	0.02	0.16	0.06	0.42	4.97	−0.04
$CorCl_5^{\cdot}$ (**2b**)	129.4	0.05	0.14	0.04	0.31	6.33	1.12
$CorBr_5^{\cdot}$ (**2c**)	162.6	0.06	0.12	0.02	0.22	6.17	1.98

Note: The atomic numbering schemes are given in Figs. 1 and 2.

account C_{5v} symmetry for all the systems with even numbers of electrons (in the case of molecules and anions) or without regard for the symmetry of the systems (radicals) (**1a—c** and **2a—c**).

$C_{60}X_5^{\cdot}$ and $CorX_5^{\cdot}$ radicals. The $C_{60}X_5^{\cdot}$ (**1**) and $CorX_5^{\cdot}$ (**2**) radicals are cyclopentadienyl type radicals. The ground states of these radicals with C_{5v} symmetry are degenerate. In view of Jan-Teller's theorem, one would expect a shift in the atomic nuclei, which would break the C_{5v} symmetry. Optimization of the geometry of radicals **1a—c** and **2a—c** without symmetry restrictions gave structures with C_s symmetry, and in systems **1a—c** and **2a—c**, the geometric parameters of the pentagons under consideration differ only slightly. These five-membered rings contain two double bonds (1.36—1.38 Å) and three single bonds (1.43—1.47 Å). In the radicals, the spin density is localized mainly on the p_z-AO of one of the atoms of the five-membered ring (0.43—0.51 and 0.54—0.56 in $CorX_5^{\cdot}$ and $C_{60}X_5^{\cdot}$, respectively; the z axis is perpendicular to the plane of this ring). Taking into account the σ- and π-contributions, the total spin populations of the pentagonal face are 0.89—0.93 and 0.94—0.95 for corannulene and fullerene derivatives, respectively. The results of calculations of the heats of formation, effective charges, and energies of HOMOs of radicals **1a—c** and **2a—c** are given in Table 1. Note that the calculated geometric and energy characteristics of radical **1a** coincide with the published data.[13]

Systems with even numbers of electrons. The results of calculations of molecules **3—6** are given in Table 2. It was found that all compounds with even numbers of electrons have closed electron shells, and the energy levels of HOMO and LUMO are substantially separated, which is indicative of the kinetic stability of the systems.

Anions. A comparative analysis of the coefficients of the AOs in the HOMO of anions **3** and **4** demonstrated that the p_z-AOs of the C atoms of the five-membered ring surrounded by CX groups make the major contribution to these MOs, and the electron density distribution in the HOMO of systems **3a—c** is virtually identical to

Table 2. Heats of formation (ΔH_f^0), energies of the highest occupied (E_{HOMO}) and lowest unoccupied (E_{LUMO}) levels, charges on the silicon atoms (q_{Si}) and the carbon atoms (q_C) of the pentagon under consideration, sums of the squares of the coefficients of the p_z-AOs of the $C^{(1)}$—$C^{(5)}$ atoms in the frontier π- and π*-MOs[a] (populations p(π) and p(π*)), and energies of π*-MOs (E_{π}^{*}) of molecules **1—6** with C_{5v} symmetry calculated by the MNDO/PM3 method

System	ΔH_f^0 /kcal mol^{-1}	Energy[b]/eV			Charge/au		Populations/au	
		$-E_{HOMO}$	E_{LUMO}	E_{π^*}	q_{Si}	$-q_C$	p(π*)	p(π)
C_{60} (**1**)	811.7	9.48^5	-2.89^3	−2.89		0.00	0.04	0.07
Cor (**2**)	142.3	8.99^2	1.03^2	0.87		0.05	0.17	0.20
$C_{60}H_5^-$ (**3a**)	642.5	4.49^2	0.38^2	5.07		0.20	0.13	0.35
$C_{60}Cl_5^-$ (**3b**)	616.0	5.46^2	-0.17^2	3.48		0.17	0.04	0.36
$C_{60}Br_5^-$ (**3c**)	662.2	5.71^2	-0.31^2	1.94		0.14	0.01	0.30
$CorH_5^-$ (**4a**)	101.8	2.85^2	4.57^2	6.50		0.20	0.20	0.34
$CorCl_5^-$ (**4b**)	48.1	4.48^2	2.59^2	4.50		0.16	0.11	0.32
$CorBr_5^-$ (**4c**)	72.6	4.93^2	1.46^2	3.90		0.13	0.08	0.29
$C_{60}H_5SiCp$ (**5a**)	758.8	8.80^2	-2.18^2	0.46	0.13			
$C_{60}Cl_5SiCp$ (**5b**)	745.1	9.13^2	-2.51^2	0.50	0.12			
$C_{60}Br_5SiCp$ (**5c**)	793.8	9.18^2	-2.58^2	0.51	0.12			
$CorH_5SiCp$ (**6a**)	190.1	7.94^2	-0.69^2	0.42	0.12			
$CorCl_5SiCp$ (**6b**)	160.2	8.53^2	-1.06^2	0.51	0.13			
$CorBr_5SiCp$ (**6c**)	190.8	8.62^2	-1.59^2	0.53	0.12			
$C_{60}SiCp^+$	1025.0	11.83^1	-5.69^1	0.62	−0.05			
$CorSiCp^+$	342.6	12.02^2	-4.91^2	0.62	0.08			

Note: The atomic numbering schemes are given in Figs. 1 and 2.

[a] π*-MO is the unoccupied orbital to which the p_z-AO of the pentagon under consideration makes the major contribution.

[b] Superscipts denote the degree of degeneracy of the energy level.

Table 3. Wiberg indices (W/au) and bond lengths (d/Å)* calculated by the MNDO/PM3 method

Complex	$W(\mathrm{Si{-}C_1})$	$d(\mathrm{Si{-}C_1})$	$W(\mathrm{C_1{-}C_1'})$	$d(\mathrm{C_1{-}C_1'})$
$\mathrm{C_{60}H_5SiCp}$ (**5a**)	0.200	2.434	1.277	1.431
$\mathrm{C_{60}Cl_5SiCp}$ (**5b**)	0.161	2.472	1.288	1.428
$\mathrm{C_{60}Br_5SiCp}$ (**5c**)	0.150	2.483	1.281	1.430
$\mathrm{CorH_5SiCp}$ (**6a**)	0.225	2.413	1.269	1.428
$\mathrm{CorCl_5SiCp}$ (**6b**)	0.166	2.467	1.283	1.422
$\mathrm{CorBr_5SiCp}$ (**6c**)	0.147	2.487	1.276	1.422

* The atomic numbering schemes are given in Figs. 1 and 2.

Table 4. Energies of the cleavage of the bonds in $\mathrm{CorX_5SiCp}$ and $\mathrm{C_{60}X_5SiCp}$[a,b] calculated by the MNDO/PM3 method

Reaction	ΔH/kcal mol^{-1}
$\mathrm{CorH_5{-}SiCp \rightarrow CorH_5^{\cdot} + SiCp^{\cdot}}$	56.4
$\mathrm{CorCl_5{-}SiCp \rightarrow CorCl_5^{\cdot} + SiCp^{\cdot}}$	65.2
$\mathrm{CorBr_5{-}SiCp \rightarrow CorBr_5^{\cdot} + SiCp^{\cdot}}$	66.9
$\mathrm{C_{60}H_5{-}SiC \rightarrow C_{60}H_5^{\cdot} + SiCp^{\cdot}}$	59.9
$\mathrm{C_{60}Cl_5{-}SiCp \rightarrow C_{60}Cl_5^{\cdot} + SiCp^{\cdot}}$	66.5
$\mathrm{C_{60}Br_5{-}SiCp \rightarrow C_{60}Br_5^{\cdot} + SiCp^{\cdot}}$	68.3
$\mathrm{CorH_5{-}SiCp \rightarrow CorH_5^{-} + SiCp^{+}}$	196.3
$\mathrm{CorCl_5{-}SiCp \rightarrow CorCl_5^{-} + SiCp^{+}}$	173.4
$\mathrm{CorBr_5{-}SiCp \rightarrow CorBr_5^{-} + SiCp^{+}}$	166.4
$\mathrm{C_{60}H_5{-}SiCp \rightarrow C_{60}H_5^{-} + SiCp^{+}}$	121.1
$\mathrm{C_{60}Cl_5{-}SiCp \rightarrow C_{60}Cl_5^{-} + SiCp^{+}}$	108.1
$\mathrm{C_{60}Br_5{-}SiCp \rightarrow C_{60}Br_5^{-} + SiCp^{+}}$	105.8

[a] $\Delta H_\mathrm{f}\,(\mathrm{C_5H_5Si^+})$ = 284.6 kcal mol^{-1}.

[b] Since the energies of homolysis for the sandwich complexes $\mathrm{C_{60}SiCp \rightarrow C_{60}^{\cdot} + SiCp^{\cdot}}$ and $\mathrm{CorSiCp \rightarrow Cor^{\cdot} + SiCp^{\cdot}}$ differ only slightly (by less than 4 kcal mol^{-1}), the differences in the energies of heterolysis should approximate the differences in the ionization potentials of $\mathrm{C_{60}X_5^-}$ and $\mathrm{CorX_5^-}$ calculated according to the Koopmans theorem. However, this is not actually the case because the Koopmans theorem is not rigorous. For example, the energies of ionization calculated for $\mathrm{CorBr_5^-}$ according to the Koopmans theorem and those determined from the heats of formation of $\mathrm{CorBr_5^-}$ and $\mathrm{CorBr_5^{\cdot}}$ differ by ~1 eV.

that observed in the fullerene analogs (**4a—c**, see Table 2). It should be also noted that the energies of the unoccupied π^*-MOs, which are to a large extent localized on the pentagon, are lower (from 2 to 6.5 eV, see Table 1) than the energies of the corresponding MOs in $\mathrm{Cp^-}$ (7.9 eV). This should cause elongation of their bonds with transition metals due to back π-donation. In the fullerene derivatives, the energies of the analogous π^*-MOs are slightly lower than those of the corresponding π^*-MOs of corannulene, and the contribution of the p_z-AOs is somewhat smaller, which is reasonably attributable to the increased length of the conjugated system of fullerene.

Sandwich complexes. The results of calculations of molecules **5a—c** and **6a—c** with the condition that C_{5v} symmetry occurs are given in Tables 2 and 3 (we used the data published in Ref. 6 in which complexes **5a—c** were considered). It was established that local minima occur on the potential energy surfaces of complexes **6a—c**. When common symmetry restrictions were removed but local C_{5v} symmetry of the $\mathrm{SiC_5H_5}$ and $\mathrm{C_{20}H_{10}X_5}$ fragments was retained, these critical points, as in the case of the $\mathrm{C_{60}X_5SiCp}$ complexes,[6] were saddle points.

A comparison of the characteristics of complexes **5** and **6** calculated for the conformation with C_{5v} symmetry and for the conformers with local C_{5v} symmetry of the above-mentioned fragments demonstrated that when symmetry restrictions were removed, the energies and charges changed only slightly. Substantial changes are observed only in the angles between the two semiaxes of the sandwich. What this means is the cyclopentadienyl fragment can be rather readily rotated with respect to the silicon atom.

A comparison of the results of calculations of the corannulene and fullerene[6] complexes leads to the following conclusions. The energies of homolysis of the $\mathrm{CorX_5{-}SiCp \rightarrow CorX_5^{\cdot} + SiCp^{\cdot}}$ and $\mathrm{C_{60}X_5{-}SiCp \rightarrow C_{60}X_5^{\cdot} + SiCp^{\cdot}}$ bonds (see Table 4) differ only slightly (by 0.4—3.5 kcal mol^{-1}), whereas the difference in the energies of heterolysis is larger (65—75 kcal mol^{-1}; Table 4). This is reasonably attributable to the difference in the ionization potentials of the $\mathrm{C_{60}H_5^-}$ and $\mathrm{CorH_5^-}$ anions or, in other words, to substantially larger electron affinity in the $\mathrm{C_{60}H_5^{\cdot}}$ radical than in $\mathrm{CorH_5^{\cdot}}$.

The structures of the corannulene sandwich complexes and the corresponding fragments of the fullerene complexes are also very similar. This is evidenced by the almost identical distances between the corresponding atoms in the corannulene and fullerene clusters containing identical X groups (see Table 3).

Like the fullerene η^5-π-complex $\mathrm{C_{60}SiCp^+}$, the corannulene η^5-π-complex $\mathrm{CorSiCp^+}$ is stabilized through the attachment of functional X groups at the α position.

Therefore, a comparison of the calculated parameters of the $\mathrm{CorX_5^-}$ and $\mathrm{C_{60}X_5^-}$ anions and the $\mathrm{CorX_5^{\cdot}}$ and $\mathrm{C_{60}X_5^{\cdot}}$ radicals demonstrated that the principal characteristics of the frontier MOs belonging to the pentagon under consideration are very similar. This is evidenced by the very close values of the effective charges as well as by the almost identical contributions of the p_z-AOs to the frontier MOs with the same symmetry. The energies of homolysis of the $\mathrm{C_{60}{-}Si}$ and $\mathrm{Cor{-}Si}$ bonds in the sandwich compounds $\mathrm{CorX_5SiCp}$ and $\mathrm{C_{60}X_5SiCp}$ have close values, and the local structures of the $\mathrm{C_{20}X_5}$ fragments differ only slightly. The above-mentioned facts suggest with certainty that calculations of complexes of corannulene derivatives with various moieties (including those with transition metals) will give reliable estimations of such values as bond strength, effective charges on atoms, and other characteristics of the corresponding fullerene analogs.

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