Physical Chemistry

Exohedral η^5-π-complexes of fullerene C_{20}

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The problem of stabilization of polyhedral carbon clusters, which do not obey the isolated pentagon rule, is discussed taking a dodecahedral fullerene C_{20} as an example. *Ab initio* MO LCAO calculations in the HF/3-21G approximation showed that fullerene C_{20} as well as its $C_{20}H_5$ hydrides with C_{5v} symmetry can form stable $2\eta^5$-π-complexes of the $CpFeC_{20}FeCp$ and $H_5C_{20}FeC_{20}H_5$ types. The energies of the η^5-Fe—C_{20} π-bonds in these complexes were compared with those of the Fe—Cp bond in ferrocene and the Fe—C_{60} bond in the η^5-π-$C_{60}H_5FeCp$ complex.

Key words: fullerene, π-complexes, radical, biradical, unpaired electron, sandwich-type transition-metal complexes, *ab initio* quantum-chemical calculations, HF/3-21G method.

Fullerenes C_n (n = 60, 70, 76, 84, *etc.*) known to date are built only of five- and six-membered rings. From the outset of fullerene chemistry, stable forms of polyhedral clusters C_n were mainly studied by theoreticians. Such fullerenes obey the so-called isolated pentagon rule (IPR).[1,2] This rule provides a qualitative explanation for the fact that the clusters built of less than 60 atoms can be formed only under specific conditions and why they can hardly be isolated. From the IPR it follows, in particular, that the presence of pentalene structures (the fragments built of two condensed five-membered rings) in the carbon cage of fullerene C_{60} leads to its destabilization compared to the isomer with I_h symmetry, in which five-membered rings are surrounded only by six-membered rings. Indeed, quantum-chemical calculations showed that the energy of the C_{60} isomer with one pentalene fragment is ~1 eV higher than that of fullerene I_h-C_{60} (see Ref. 2).

Delocalized conjugated π-electron systems of fullerenes involve the atoms of all five- and six-membered rings. However, even such a fullerene as I_h-C_{60} is not prone to formation of stable η^5- and η^6-complexes. The situation changes significantly in the case of cyclopentadienyl type derivatives of C_{60} or C_{70}. As was shown theoretically, attachment of univalent functional groups R (*e.g.*, H, Cl, and Br atoms, *etc.*[3,4,6—10]) to C atoms in the α-positions relative to the same five-membered ring (*pent**) favors stabilization of η^5-π-complexes of the $L_nMC_{60}R_5$ type (L is ligand). In these complexes, the atom M is coordinated to the *pent** face. According to the estimates obtained from PM3 calculations, the energies of the M—*pent** bonds in the complexes η^5-π-$C_{60}R_5MCp$ and $2\eta^5$-π-$M(C_{60}H_5)_2$ (M = Si, Ge, Sn) are close to those of the corresponding M—Cp bonds in the classical sandwich compounds MCp_2 (see Refs. 9, 10). *Ab initio* HF/3-21G calcula-

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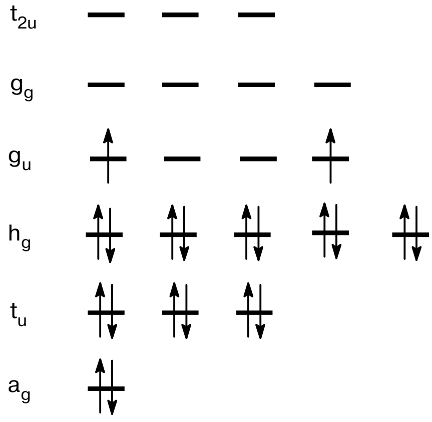
tions[10] of systems with M = Fe, Si have lead to similar results.

The above-mentioned procedure for generating stable η^5-π-complexes of fullerene derivatives was confirmed experimentally. For instance, a pentaphenyl fullerene derivative, $C_{60}Ph_5{}^{\bullet}$ radical, and its η^5-complexes with metal atoms (M = Li, In, Tl) were synthesized. X-Ray study[5] of the complex with M = Tl confirmed that this system has a half-sandwich η^5-π-structure. A similar procedure for stabilization of η^5-π-complexes of fullerene C_{60} derivatives (see Refs. 4 and 6—10) can also be used for the fullerenes C_{70}, C_{40}, and their analogs containing heteroatoms.[11—14] In addition to exohedral complexes, sufficiently stable endohedral complexes such as D_{5d}-Fe@$C_{40}H_{10}$ and D_{5d}-Fe@$C_{40}H_{30}$, which are polyhedral analogs of the ferrocene molecule,[12] can also be formed. Mention may be made that it is also possible to stabilize η^5-π-complexes of fullerenes by attaching appropriate species (*e.g.*, MCp with M = Si, Fe) to all 12 pentagonal faces of their carbon cages in a η^5-manner.[8]

Among convex polyhedral carbon clusters built only of pentagons and hexagons, dodecahedral fullerene C_{20} is the most strained. The possibility of the existence of this structure was first discussed in the early 1970s.[15,16] A scheme of the one-electron energy levels of the cluster I_h-C_{20}, obtained from calculations by the Hückel method[16] is shown below.

Scheme 1



In particular, from Scheme 1 it follows that cluster C_{20} must be an open-shell system, have the triplet ground state, and that its symmetry must differ from that of a regular dodecahedron (I_h) due to the Jahn—Teller distortion.

In particular, the results of the *ab initio* MO LCAO SCF calculations of cluster C_{20} carried out with rather large basis sets[17] confirmed qualitative conclusions about the electronic structure of fullerene C_{20}. It was shown that the $^3A_{2g}$ state with D_{5d} symmetry is the ground state of cluster C_{20}.

Quantum-chemical calculations of cyclic, bowl-shaped, and polyhedral isomers of cluster C_{20} have also been carried out using the density functional approach.[18—20] However, no unambiguous conclusion about the most stable isomer can be drawn based on the results of these and previously reported calculations.[17] Mention should be made of (i) a recent study[22] in which the possibility of the existence of polyhedral heteroatomic analogs of C_{20} (namely, the Si_{20} and Ge_{20} clusters) is discussed and (ii) of experimental studies[23,24] carried out prior to the discovery of fullerenes and containing the description of a procedure for the synthesis of saturated molecules $C_{20}H_{18}Me_2$ and $C_{20}H_{20}$ with polyhedral (dodecahedral) carbon cage.

In transition-metal chemistry, unstable organic species are known to be ligands in some rather stable organometallic complexes. For instance, a stable complex of irontricarbonyl with cyclobutadiene exists, though no synthesis of this hydrocarbon has been reported to date. Despite the pentalene molecule is unstable under normal conditions, stable sandwich complexes of Ti, Zn, an Hf with pentalene are also known to exist.[25]

These examples show that, in principle, unstable fullerenes can be used as ligands in complexes with transition metals. It should also be taken into account that the fullerenes C_n can form not only exohedral, but also endohedral complexes M@C_n, in which the metal atom can inhibit kinetic activity of the unstable carbon cage.

The aim of this work was to study the possibility of stabilization of the dodecahedral fullerene C_{20} by forming exohedral complexes with some ligands.

Calculation Procedure

It is well known (see, *e.g.*, Refs. 26, 27) that the Hartree—Fock calculations of transition-metal complexes can best be carried out using the Møller—Plesset perturbation theory with rather large basis sets. In this work, we are interested only in the relative values of the energy and geometric parameters of the complexes under study, whose structures contain more than 40 atoms including one or two Fe atoms. Therefore, we used the 3-21G basis set[28] for both C and Fe atoms. The use of this basis set provides a compromise between the accuracy of calculations and computational cost. Calculations were carried out by the HF/3-21G method using the GAMESS program package[29] (on a DEC 3000 AXP-400X workstation) and PC GAMESS [30] (on a personal computer with a PENTIUM®-III CPU). Open-shell systems were calculated in the ROHF approximation.

The geometries and electronic structures of the complexes under study were simulated taking into account the restrictions imposed by the C_s, C_{5v}, D_{5h}, or D_{5d} symmetry groups. Then, the characters of the stationary points found under these conditions were refined by performing additional calculations with full geometry optimization. Here, a number of different asymmetric structures obtained from the structures found in the above-mentioned calculations by small displacements of the positions of particular atoms were used as initial approximations. If the results of calculations of a particular structure converged to those obtained assuming conservation of the symmetry, the

Table 1. Energy characteristics of fullerene C_{20} and its ions, $C_{20}{}^q$, with different multiplicities (m) calculated by the RHF and ROHF/3-21G methods

Structure	q^a	m	Symmetry	$-E_{tot}{}^b$	$E_{HOMO}{}^c$	$E_{LUMO}{}^d$
				au		
1	+2	1	I_h	751.6330	−0.7034	−0.3967
2a	0	1	C_{2h}	752.3057	−0.2745	−0.0316
2b	0	3	C_s	752.3090	−0.1533	−0.0358
2c	0	3	C_{2h}	752.2980	−0.1524	−0.0460
2d	0	3	D_{5d}	752.2972	−0.1521	−0.0444
3	−1	2	C_s	752.3645	0.0228	0.1533
4a	−2	5	I_h	752.2374	0.0217	0.3643
4b	−2	1	D_{5d}	752.2426	−0.0908	0.3405

[a] Ion charge.
[b] The total energy.
[c] The highest occupied MO energy.
[d] The lowest unoccupied MO energy.

corresponding stationary point was interpreted as a local minimum.

Results and Discussion

Fullerene C_{20}. The energy characteristics of fullerene C_{20}, its dication and differently charged anions obtained in this work for the states with different multiplicities are listed in Table 1. As was mentioned above, neutral fullerene I_h-C_{20} must be an open-shell system with the quadruply degenerate highest occupied one-electron energy level filled with two electrons. However, the corresponding dication I_h-$C_{20}{}^{2+}$ (**1**) must be a closed-shell system with a quintuply degenerate highest occupied energy level. The neutral cluster C_{20} must have the triplet ground state with a reduced symmetry.[17] From the data listed in Table 1 it follows that the ground state of C_{20} has a C_s symmetry (structure **2b**, Fig. 1) rather than a higher D_{5d} symmetry (structure **2d**), as was stated earlier.[17] In addition, the energy of fullerene C_{20} in the singlet state with C_s symmetry (**2a**) was found to be only 2.1 kcal mol^{-1} higher than that of the corresponding triplet state **2b** (see Table 1).

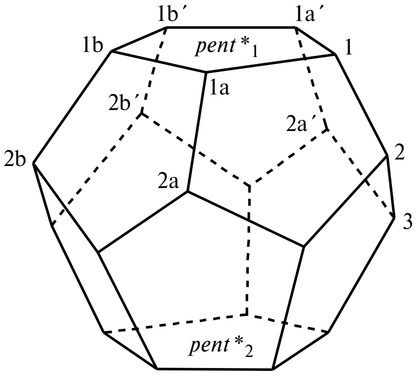


Fig. 1. Structure of fullerene C_{20} and its ions, $C_{20}{}^q$, with dodecahedral topology; the geometric parameters of singlet $C_{20}{}^{2+}$ with I_h symmetry (**1**), C_{20} with C_s symmetry (**2a**), and $C_{20}{}^{2-}$ with D_{5d} symmetry (**4a**); doublet $C_{20}{}^-$ with C_s symmetry (**3**); triplet $C_{20}{}^-$ with C_s symmetry (**2b**), C_{20} with D_{2h} symmetry (**2c**), C_{20} with D_{5d} symmetry (**2d**); and quintet $C_{20}{}^{2-}$ with I_h symmetry (**4b**) are listed in Table 2.

According to ROHF/3-21G calculations, there is yet another local minimum on the PES corresponding to structure **2c** of cluster C_{20} with D_{2h} symmetry. The geometric parameters of clusters **1** and **2a—d** are listed in Table 2. In the triplet clusters **2b—d**, the spin population is mainly localized on the atoms of two polar faces. In each of the *pent*$^*{}_i$ faces of cluster **2c** (see Fig. 1), it is concentrated (0.81 au) on one C atom. Therefore, this cluster must be prone to formation of a σ-bond. Only in cluster **2d** is the spin population distributed uniformly over the atoms of the polar faces (0.15 au on each atom of the C(1) type) and over the atoms lying on the lateral surface (0.05 au on each atom of the types C(2) and C(3)). Therefore, only cluster **2d** can be coordinated by an appropriate functional group in a η^5-fashion. The unpaired electrons of this cluster occupy two MOs with e_1 symmetry, which are mainly composed of the π-orbitals of the C atoms of the polar faces (the upper polar face, *pent*$^*{}_1$, and the lower polar face, *pent*$^*{}_2$, see Fig. 1). Thus, formally, one unpaired electron is localized on each polar face of cluster **2d** and these faces can be considered as analogs of the cyclopentadienyl radical (Cp radical). Therefore, isomer **2d** can be prone to formation of *exo*-2η^5-π-complexes. This is not typical of fullerenes C_{60} and C_{40}, since their triplet biradical states, in which the spin populations are also localized over polar faces, *pent** posses high energies. Carbon-carbon bonds in the Cp radical have different length; in contrast to this, all C—C bonds in the *pent** cycles of fullerene **2d** are of the same length.

Sandwich-type transition-metal complexes are characterized by partial transfer of the electron density from the central atom to ligands. Therefore, when considering fullerene C_{20} as a potential η^5-ligand, it is of interest to calculate the geometry and electronic structure of the radical anion $C_{20}{}^{\bullet -}$ (**3**) and the electron affinities of different isomers of fullerene C_{20}. According to calculations, radical anion **3** in the ground state has a C_s symmetry and a multiplicity of 2. Isomers **2a—d** possess rather high electron affinities, namely, 1.60 (**2a**), 1.51 (**2b**), 1.81 (**2c**), and 1.83 eV (**2d**). In radical anion **3**, the spin population and negative charge are to a greater extent localized on the atoms of the polar faces *pent*$^*{}_1$ (0.68 and −0.37 au, respectively) and *pent*$^*{}_2$ (0.17 and −0.26 au, respectively) with predominant contribution of the upper face *pent*$^*{}_1$ (see Fig. 1). The geometric parameters of radical anion **3** are listed in Table 2. There is one short bond similar to the double bond on each of the *pent*$^*{}_1$ and *pent*$^*{}_2$ faces. Two bonds on the *pent*$_1$ face are quite similar to ordinary bonds. No ordinary bonds were found on the *pent*$_2$ face.

The $C_{20}{}^{2-}$ dianion was calculated in the ROHF/3-21G approximation both in the singlet (struc-

Table 2. Bond lengths (d) and Mulliken bond orders (au, numbers in brackets) in fullerene C_{20} and its ions, $C_{20}{}^q$, with different multiplicities (m) calculated by the RHF/3-21G method

Structure	q^a	m	Symmetry	d/Å				
				C(1)—C(1a)[b]	C(1a)—C(1b)	C(1b)—C(1b′)	C(1)—C(2)	C(2)—C(3)
1	+2	1	I_h	1.440	1.440	1.440	1.440	1.440
				[1.120]	[1.120]	[1.120]	[1.120]	[1.120]
2a	0	1	C_{2h}	1.408	1.486	1.379	1.538—1.438	1.408—1.437
				[1.282]	[1.038]	[1.450]	[0.952—1.150]	[1.282—1.150]
2b	0	3	C_s	1.526	1.365	1.489	1.514—1.479	1.410—1.430
				[0.941]	[1.509]	[0.998]	[0.944—1.034]	[1.267—1.199]
				1.432 [c]	1.447 [c]	1.397 [c]	1.477—1.488 [c]	
				[1.217]	[1.148]	[1.343]	[1.065—1.028]	
2c	0	3	C_{2h}	1.450	1.408	1.465	1.475—1.466	1.423—1.429
				[1.134]	[1.293]	[1.085]	[1.065—1.081]	[1.207—1.196]
2d	0	3	D_{5d}	1.430	1.430	1.430	1.481	1.421
				[1.209]	[1.209]	[1.209]	[1.050]	[1.212]
3	−1	2	C_s	1.409	1.504	1.372	1.483—1.527	1.413—1.435
				[1.314]	[1.012]	[1.519]	[1.047—0.979]	[1.291—1.172]
				1.414 [c]	1.488 [c]	1.371 [c]	1.468—1.532 [c]	
				[1.300]	[1.047]	[1.524]	[1.060—0.967]	
4a	−2	1	I_h	1.450	1.450	1.450	1.450	1.450
				[1.175]	[1.175]	[1.175]	[1.175]	[1.175]
4b	−2	5	D_{5d}	1.424	1.424	1.424	1.527	1.411
				[1.310]	[1.310]	[1.310]	[0.985]	[1.286]

[a] Ion charge.

[b] The numbering of atoms is shown in Fig. 2.

[c] The characteristics of the lower hemisphere of fullerene C_{20}.

ture **4a** with D_{5d} symmetry) and quintet (structure **4b** with I_h symmetry) state (see Table 1). Calculations also revealed local minima on the corresponding PES; however, the isomers **2a—d** of cluster C_{20} were found to have negative affinities to the second electron.

It should be noted that the unpaired electrons of dianion **4b** fill two MOs with e_{1u} symmetry, which are mainly composed of the π-orbitals of the atoms of polar pentagonal faces *pent*$^*{}_1$ and *pent*$^*{}_2$, and two MOs with e_{2u} symmetry, which are mainly composed of the π-orbitals of the atoms lying on the lateral surface. Thus, dianion **4b** with the multiplicity 5 can form four multi-center bonds. These are two η^5-*exo*-bonds (or η^5-*endo*-bonds) involving the atoms on the polar faces and two bonds (likely, only of the *endo*-η^5-type) involving the atoms lying on the lateral area. By I_h symmetry, all the atoms in dianion **4b** are equivalent, namely, the distance from each atom to the center of symmetry (R) is 2.032 Å and the effective charge and spin population on each atom are −0.10 and 0.20 au, respectively. The excitation energy corresponding to the transition **4a** → **4b** is only 3.3 kcal mol^{-1}.

Exohedral complexes. Qualitative analysis (see above) suggested that biradical **2d** with two unpaired electrons localized on the multi-center MOs of the C atoms of the polar pentagonal faces can form two η^5-bonds with appropriate ligands. To prove this assumption, we performed *ab initio* HF/3-21G calculations of exohedral complexes CpFe—C_{20}—FeCp (**5**), H_5C_{20}—Fe—$C_{20}H_5$

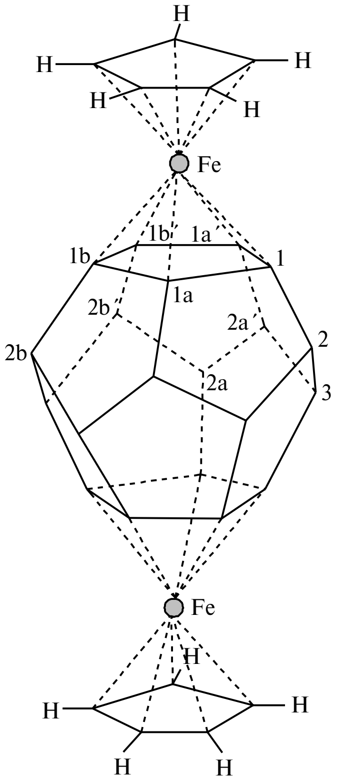


Fig. 2. Structure of complex $2\eta^5$-π-CpFeC_{20}FeCp (**5**) with D_{5d} symmetry.

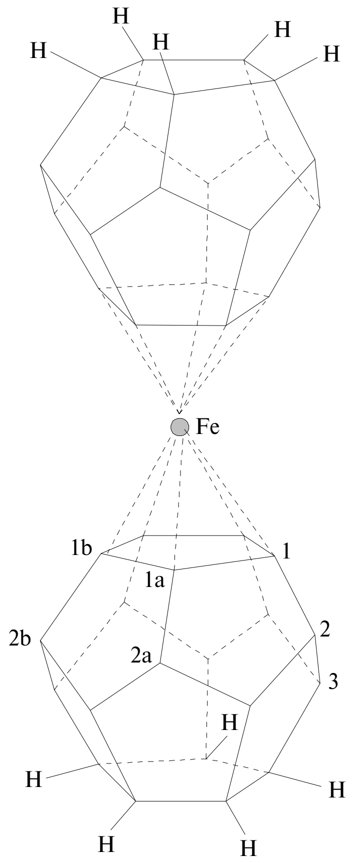


Fig. 3. Structure of complex 2η^5-π-$H_5FeC_{20}H_5$ (**6**) with D_{5d} symmetry.

(**6**), $C_{20}H_5$—Fe—H_5C_{20} (**7**), and CpFe—$C_{20}H_{10}$—FeCp (**8**) assuming D_{5d} symmetry (Figs. 2 and 3). The results of calculations are listed in Tables 3 and 4.

Complex **5** (see Fig. 2) was found to have the singlet ground state. The energy of the Fe—*pent** bond in this complex estimated using the formula $\Delta E = 0.5[E_{tot}(\mathbf{2d}) + 2E_{tot}(\mathrm{FeCp}) - E_{tot}(\mathbf{5})]$ (E_{tot}(X) is the total energy of the species X) is 76 kcal mol^{-1}. This is lower than the energies of the corresponding bonds in the complexes $C_{60}H_5FeCp$ and $FeCp_2$ (117 and 110 kcal mol^{-1}, respectively) calculated[10] in the same approximation. Because of this, the Fe—C_{pent*} distances are somewhat longer than the corresponding Fe—C_{Cp} distances; however, the total bond orders, p(Fe—C_{20}), are rather high (0.770 au, *cf.* 1.095 au for p(Fe—C_{Cp})), which also indicates a strong Fe—*pent** bond. The energy of complex **5** in the triplet state is 20 kcal mol^{-1} higher than that of the complex in the singlet state. The effective charges on the Fe atoms in complex **5** are 1.5 au. The electron density is transferred from these atoms to a greater extent to the C_{20} cage (−0.85 au from each Fe atom) and to a lesser extent to the Cp radical (−0.60 au). As a result, a negative charge of −1.70 au is concentrated on the cluster C_{20}.

In complex **6** (see Fig. 3), the Fe—C_{pent*} bond is somewhat longer than the corresponding bond in structure **5**; on the other hand, the total order of this bond, p(Fe—*pent**) = 0.790 au, is somewhat higher. In this complex, the electron density transfer from the Fe atom to each carbon cage (0.805 au) is nearly the same as in complex **5**. To determine the energy of the Fe—*pent**

Table 3. Results of RHF/3-21G calculations of exohedral complexes of fullerene C_{20}, ferrocene molecule, and their fragments

Structure	Symmetry	$-E_{tot}{}^a$	$E_{HOMO}{}^b$	$E_{LUMO}{}^c$	$\Delta E\,^d$ /kcal mol^{-1}	$q\,^e$/au				
		au				Fe	C(1) [*pent**]	C(2)	C(3)	C(4)
5	D_{5d}	3647.1707	−0.2671 (e_{2u})	0.0014 (e_{1u})	75.8	1.48	−0.17	0.00	—	—
FeCp$^•$	C_{5v}	1447.3158	−0.0819 (a_1)	0.0534 (e_1)	—	0.65	−0.40	—	—	—
FeCp$^•$ [10]	C_s	1447.5362	−0.0889 (a′)	0.0526 (a′)	—	0.59	−0.37±0.02	—	—	—
$FeCp_2$ [10]	D_{5d}	1638.5937	−0.3343 (e_{2g})	0.1237 (e_{2u})	110.4	1.38	−0.40	—	—	—
6	D_{5d}	2767.2761	−0.2753 (e_{1g})	0.0523 (e_{2g})	58.3 45.0	1.61	−0.17	−0.26	—	—
$C_{20}H_5{}^-$	C_{5v}	755.3220	−0.0995 (e_1)	0.2025 (e_2)	—	—	−0.10	−0.01	−0.06	−0.24
$C_{20}H_5{}^+$	C_{5v}	754.7401	−0.3685 (e_2)	−0.2803 (a_1)	—	—	0.07	0.02	0.05	−0.20
6a	C_s	755.4885	−0.2644 (a′)	−0.1376 (a″)	—	—	[−0.08]	[−0.34]	[0.42]	−0.26
6b	C_s	2011.7159	−0.1124 (a′)	0.209 (a″)	—	0.74	-0.72^{1f} -0.04^{2f} 0.03^{2f}			
7	D_{5d}	2766.7459	−0.1982 (a_{1u})	−0.1378 (e_{1g})	—	1.70	−0.13	−0.36	0.08	−0.02
8	D_{5d}	3652.7871	−0.1159 (e_{2u})	−0.0215 (e_{2g})	−125	1.56	−0.15	−0.27	—	—
8a (T)	D_{5d}	758.5389	−0.1566 (e_{2u})	0.1057 (e_{1u})	—	—	0.02	−0.27	—	—
8a (S)	D_{5d}	758.1778	−0.2402 (e_{1u})	−0.1981 (a_{1u})	—	—	−0.02	−0.22	—	—

[a] Total energy.

[b] The highest occupied MO energy (the symmetry of the HOMO is given in parentheses).

[c] The lowest unoccupied MO energy (the symmetry of the LUMO is given in parentheses).

[d] The bond energy Fe—*pent** (or Fe—Cp).

[e] The charges on the atoms (faces, or layers).

[f] The upper indices mean the multiplicities of the given values.

Table 4. Bond lengths (*d*) and Mulliken bond orders (au, numbers in brackets) in exohedral complexes of fullerene C_{20}, ferrocene molecule, and their fragments calculated by the RHF/3-21G method

Structure	*d*/Å						
	Fe—C$_{pent*}$	Fe—C$_{Cp}$	C(1)—C(1a)	C(1)—C(2)	C(2)—C(3)	C(3)—C(4)	C(4)—C(4a)
5	2.307	2.206	1.419	1.510	1.415	—	—
	[0.154]	[0.219]	[1.217]	[1.023]	[1.286]		
$FeCp^{\bullet}$	—	2.232	1.415	—	—	—	—
		[0.210]	[1.292]				
$FeCp_2$ [10]	—	2.204	1.417	—	—	—	—
		[0.205]	[1.256]				
6	2.316	—	1.425	1.495	1.402	1.543	1.576
	[0.158]		[1.196]	[1.061]	[1.280]	[0.922]	[0.879]
$C_{20}H_5^-$	—	—	1.426	1.505	1.401	1.545	1.580
			[1.279]	[1.014]	[1.279]	[0.929]	[0.883]
$C_{20}H_5^+$	—	—	1.520	1.336	1.515	1.473	1.624
			[0.912]	[1.593]	[0.969]	[1.020]	[0.799]
7	2.272	—	1.406	1.528	1.571	1.417	1.427
	[0.155]		[1.253]	[0.905]	[0.894]	[1.186]	[1.146]
8	2.173	2.288	1.406	1.488	1.632	—	—
	[0.222]	[0.170]	[1.205]	[0.948]	[0.901]		

Table 5. Bond lengths (*d*) and Mulliken bond orders (au, numbers in brackets) in the fragments of exohedral complexes of fullerene C_{20} calculated by the RHF/3-21G method

Structure	*d*/Å						
	C(1)—C(1a)	C(1a)—C(1b)	C(1b)—C(1b′)	C(1)—C(2)	C(2)—C(3)	C(3)—C(4)	C(4)—C(4a)
6a	1.414	1.494	1.368	1.508—1.490	1.398—1.401	1.540—1.546	1.578
	[1.280]	[1.039]	[1.516]	[1.014—1.023]	[1.279—1.263]	[0.921—0.922]	[0.878]
8a (T)	1.409	1.409	1.409	1.493	1.608	—	—
	[1.266]	[1.266]	[1.266]	[0.936]	[0.873]		
8a (S)	1.390	1.390	1.390	1.478	1.705	—	—
	[1.350]	[1.350]	[1.350]	[0.934]	[0.713]		

bond, we calculated structural fragments of complex **6**, namely, the radicals $H_5C_{20}^{\bullet}$ (**6a**) and $H_5C_{20}Fe^{\bullet}$ (**6b**). Preliminary calculations of the ions $H_5C_{20}^+$ and $H_5C_{20}^-$ showed that they have closed electron shells (see Table 3) and structures with a C_{5v} symmetry. The cation was found to have a nondegenerate lowest unoccupied energy level (the LUMO with a_1 symmetry). "Doping" of the cation $H_5C_{20}^+$ with two electrons to give the anion $H_5C_{20}^-$ leads to a change in the order of the MOs, so that the HOMO appears to be the orbital with e_1 symmetry. This orbital is completely filled (the a_1 MO is vacant), therefore, the symmetry of radical **6a** must be reduced (down to C_s) due to the Jahn—Teller effect. The change in the order of the MO levels is due to the essential changes in the geometry on going from the $H_5C_{20}^+$ cation to $H_5C_{20}^-$ anion. The bonds between the C(1) and C(2) atoms in the cation are double, whereas those in the anion are ordinary. And *vice versa*, the bonds between the C(2) and C(2′) atoms are shortened on going from the cation to the anion. The lengths of the bonds between the atoms C(2) and C(3), as well as the atoms C(3) and C(3′), also change substantially (see Table 4). The spin population on the atoms of the *pent** face in complex **6a** is higher than in the triplet cluster C_{20} (**2d**) (Table 5 and 6). Therefore, one should expect that complex **6a** can form a stronger bond of the η^5-type. The energy of homolytic dissociation of the Fe—*pent** bond in complex **6** (calculated as the heat of reaction **6** → **6a** + **6b**) is 58 kcal mol^{-1}. This is 18 kcal mol^{-1}

Table 6. The spin population (ρ/au) on the polar faces (*pent**) and lateral area (la) in radicals and biradicals

System	Symmetry	ρ(*pent**)*	ρ[C(1)]	ρ[C(1a)]	ρ[C(1b)]	ρ(la)
$^{\bullet}C_{20}^{\bullet}$ (**2d**)	D_{5d}	0.76, 0.76	0.15	0.15	0.05	0.48
$C_{20}^{-\bullet}$ (**3**)	C_s	0.68, 0.13	0.02	0.31	0.02	0.19
$H_5C_{20}^{\bullet}$ (**6a**)	C_s	0.85	0.01	0.35	0.07	0.15
$^{\bullet}C_{20}H_{10}^{\bullet}$ (**8a**)	D_{5d}	0.86, 0.86	0.17	0.17	0.17	0.28
$H_5C_{60}^{\bullet}$ [10]	C_s	0.95,	0.71	0.01	0.11	0.05
$Cp^{\bullet}$ [10]	C_s	1.00	0.64	0.02	0.16	—

* The second value corresponds to the lower face *pent**$_2$.

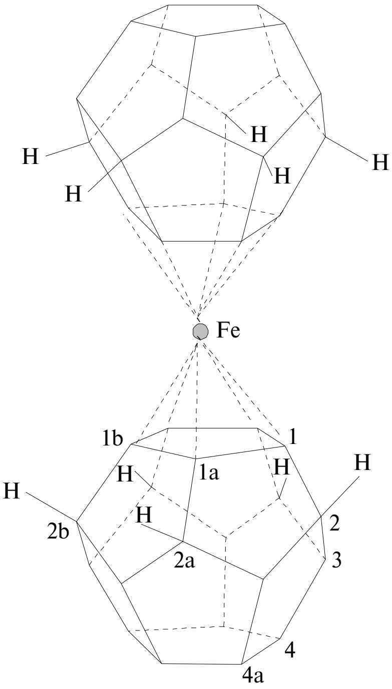


Fig. 4. Structure of complex $2\eta^5$-π-$C_{20}H_5FeH_5C_{20}$ (**7**) with D_{5d} symmetry.

lower than in complex **5**, since the Fe atom in structure **6b** is not coordinated to the center of the *pent** face).

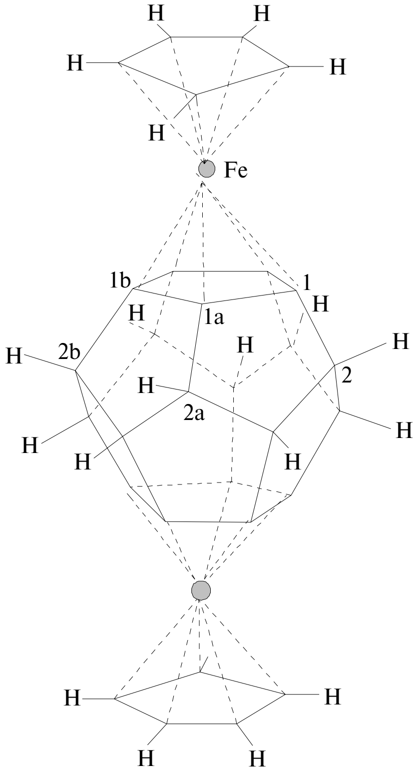


Fig. 5. Structure of complex $2\eta^5$-π-$CpFeC_{20}H_{10}FeCp$ (**8**) with D_{5d} symmetry.

In structure **7** (Fig. 4), the Fe—C_{pent*} bonds (2.272 Å) are appreciably longer than the corresponding bonds in the ferrocene molecule; however, the total order of the Fe—*pent** bond (0.775 au) is rather high.

A salient feature of structure **8** (Fig. 5) is that the Fe—C_{pent*} bonds were found to be shorter than the corresponding Fe—C_{Cp} bonds in the ferrocene molecule (2.173 *vs.* 2.204 Å, respectively). However, the Fe—C_{Cp} bonds in complex **8** are appreciably longer (2.288 Å) than in ferrocene. This leads to a substantial exothermic effect of the reaction **8** → **8a** + **8b**. The effective charge on the Fe atom (1.56 au) is comparable in magnitude with the corresponding values for other complexes (see Table 3). Analogously, the spin population on the *pent** face in the fragment **8a** is comparable with the corresponding values for the radicals and biradicals listed in Table 6.

Thus, the results of our calculations suggest that complexes **5** and **6** are stable systems with high energies of the Fe—*pent** bonds. The formation of complexes **7** and **8** from the corresponding fragments is energetically unfavorable; however, the Fe—C_{pent*} bonds in structure **8** (2.173 Å) were found to be shorter than the corresponding bonds in ferrocene molecule (2.204 Å). In addition, the results of calculations of complexes **5—8** suggest the possibility for fullerene analogs of multidecker sandwich compounds, namely, polymers of the types $(\text{—FeC}_{20}\text{—})_n$ or $(\text{—FeH}_5\text{C}_{20}\text{H}_5\text{—})_n$, to exist.

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