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ANALYSIS OF THE CHEMICAL BOND IN THE METALLOCENE USING DENSITY FUNCTIONAL THEORY

Abstract. In this work the optimization of metallocene molecular geometry by two different functional density methods has been carried out. Obtained structural and spectral data have been compared with experimental values. The donor-acceptor and dative interactions in the formation of metallocenes have been studied on the basis of the natural valence orbitals method. The ionicity and covalency of bonds between the metal atoms and carbon have been determined with use of energy partitioning analysis.

Keywords: density functional theory, metallocenes, donor-acceptor and dative interaction, covalence of bond.

Introduction.

Metallocenes are organic compounds formed mainly by transition metal and cyclopentadiene [1, 2]. The molecules of metallocenes have the form of "sandwich": a metal ion having an oxidation + 2 is situated between two parallel cyclopentadienyl rings at an equal distance from them. In various metallocenes metal-ligand bond may have either covalent or ionic character. The relative positions of the cyclopentadienyl ring depend on the compounds and form a prismatic or antiprismatic configuration.

A perennial metallocenes study showed that they have a wide practical applicability. In this case both practical and theoretical interest directly represent molecular complexes based on ferrocene, derivatives thereof, allowing to obtain chelate compounds, a number of heterometallic derivatives. Along with the metallocene containing polymer, they are used as semiconducting materials in electronics, catalysts in organic synthesis and the etc. Systems containing several metals within a single molecule are of interest and a model for the development of the general theory of exchange interactions. There is information, that chelate transition metal complexes containing ferrocene moiety were catalysts for polymerization of styrene along with other chelates based on π -complex.

The aim of this work is to investigate the nature of chemical bonds in molecules metallocene using quantum chemical density functional calculations.

Materials and methods.

All calculations were performed using GAUSSIAN'03 standard software package [3]. For carrying out the theoretical research, there was used quantum-chemical density functional method (DFT, Density Functional Theory). Calculations performed by the hybrid density functional B3LYP, with the exchange functionality Beke (B3) [4] and correlation functional of Lee, Yang and Couple (LYP) [5]. For all atoms used as a fully electronic basis set 6-31G (d). The structure of the calculations were fully optimized, no imaginary vibrational frequencies confirmed their stationary character. Furthermore, optimization of metallocene the gas phase was performed using the Amsterdam Density Functional (ADF) [6], which uses Slater functions. We used bp86/TZ2P+ method, which usually yields better results than the B3LYP/6-31G(d).

Results and discussion.

Comparison of geometric parameters

We calculated a large number of metallocene molecules with metals in the oxidation state +2. Optimized structures have D_{5d} symmetry and are in the eclipsed conformation, which is consistent with literature data.

We compared the experimental values of lengths of C-C and C - Fe bonds, obtained by gas-phase electron diffraction [7, 8] with calculated by both methods (Table. 1).

The table 1 shows that the structure which optimized at ADF, giving the C-Fe bond length lower than the experimental value at 0,016 E. In the same time structure, resulting in the program Gaussian gives bond length 2,052 E, which corresponds to the experimental value. Besides Gaussian shows all carbon-carbon bonds identical (1,428), while giving ADF spread 1,421-1,434 E, which is inconsistent with the experimental data.

Table 1 – Experimental and calculated by the B3LYP/6-31G(d) and bp86/ TZ2P+ C-C and C-Fe bond lengths in ferrocene, E

	Experiment	ADF bp86/TZ2P+		Gaussian B3LYP/6-31G(d)		
	Fe(C ₅ H ₅) ₂	Cp	Fe(C ₅ H ₅) ₂ S = 0	Cp	Fe(C ₅ H ₅) ₂ S = 0	Fe(C ₅ H ₅) ₂ S = 2
C–C	1,42 ± 0,01	1,383–1,434	1,421–1,434	1,414	1,428	1,421–1,429
C–Fe	2,06 ± 0,01	–	2,044	–	2,052	2,232–2,370
C–H	–	1,092	1,086	1,09	1,082	1,083

It is known that iron atom may be in high- and low-spin state. The calculated energy gap between high- and low-spin states of ferrocene is 19 kcal/mol. According to the literature, this difference greater than 40 kcal/mol. In the high- spin ferrocene symmetry rings are broken, they go out of parallel planes. Thus the Fe-C bond lengths increase and significantly distorted. They were also calculated metallocenes comprising not only the transition metal but and non-transition elements. The calculated by two methods experimental bond lengths are given in the Table 2.

Table 2 – Lengths of metal-carbon bonds and carbon-carbon

The metallocene	Bond	experiment	Gaussian	ADF
Pb(C ₅ H ₅) ₂	Pb–C	2,778	2,777	2,770
	C–C	1,430	1,419	1,415
Sn(C ₅ H ₅) ₂	Sn–C	2,706	2,727	2,646
	C–C	1,431	1,419	1,420
Be(C ₅ H ₅) ₂	Be–C	1,93	2,05	2,04
	C–C		1,418	1,415
Ni(C ₅ H ₅) ₂	Ni–C	2,196	2,132	
	C–C	1,430	1,408	
Co(C ₅ H ₅) ₂	Co–C	2,119	2,130	
	C–C	1,429	1,421	
Ti(C ₅ H ₅) ₂ Cl ₂	Ti–C	2,372	2,394	2,384
	C–C	1,397	1,407	1,407
Mn(C ₅ H ₅) ₂	Mn–C	2,383	2,256	2,056
	C–C	1,429	1,426	1,429
Cr(Bz) ₂	Cr–C	2,150	2,155	2,107
	C–C	1,423	1,418	1,415
Cr(Bz)(CO) ₃	Cr–C	2,208	2,229	2,172
	C–C	1,417	1,413	1,412

For all metallocene observed good the correlation between the experimental and calculated in the programs of Gaussian and ADF bond lengths of the metal - ring (Fig 1, 2.).

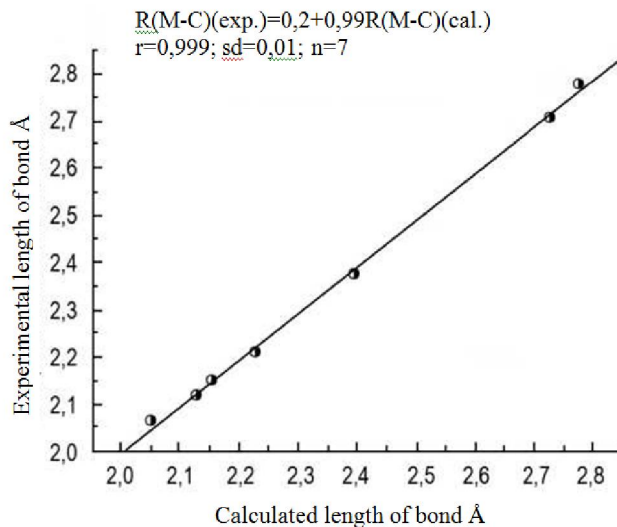


Figure 1 – The relationship between the experimental and calculated by B3LYP/6-31G(d) bond lengths in the metallocene

C-C distances in cyclopentadienyl are approximately the same in all complexes. The difference between C-C bond length from cyclopentadienyl to metallocenes about 0,014 E. This suggests that part of the π -electron density passes from C-C bonds to the C-Fe and the multiplicity of bond decreases.

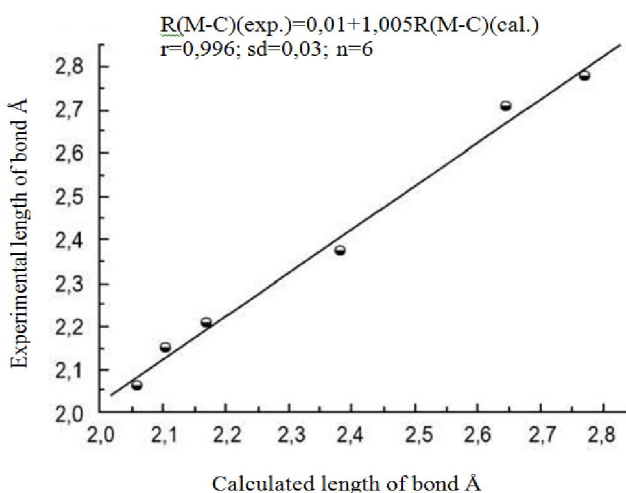


Figure 2 – The relationship between the experimental and calculated by BP86/TZ2P+ bond lengths in the metallocene

Along with changes in bond lengths should change also the effective charges on atoms as a result of electron density transfer from the ligand to the metal and conversely. We have analyzed seven different types of charges in a molecule of ferrocene (Table. 3). We used three Gaussian calculated schemes and four - from ADF. We can see from Table. 3 that the the Mulliken charges from Gaussian have similar values all carbon and hydrogen atoms, respectively, and the charge on the Fe atom is 0.556, which correlates reasonably well with the experimental results.

All experimental methods are predicting charge on the iron atom in the range of 0.6 - 1.4 e. The same regularity can also be seen with the natural charges (NBO calculation) for Fe atom charge is 1.023.

The scheme of charge distribution by Voronoi, Hershfield and multiplicity charges show different charges on the hydrogen atoms and, most importantly, carbon atoms, which can not but cause concern. Moreover, the charge on the iron atom in these schemes close to zero (-0.037, 0.049, 0.096 respectively), which do not correspond to experiment.

Table 3 – The charges on the atoms in ferrocene, calculated in the program ADF and Gaussian

Atom	Gaussian			ADF			
	Mulliken atomic charges	APT	NBO Natural charge	Mulliken atomic charges	Hirshfeld charge analisis	Voronoi charges	Multiplet charges
C	-0,205	0,042	-0,358	0,280–0,283	-0,057 – – 0,065	-0,070 – – 0,077	-0,207 – – 0,256
H	0,149	0,029	0,256	-0,292 – – 0,310	0,056–0,057	0,075–0,079	0,218–0,232
Fe	0,557	-0,714	1,023	0,225	0,049	-0,037	0,096

NMR spectra

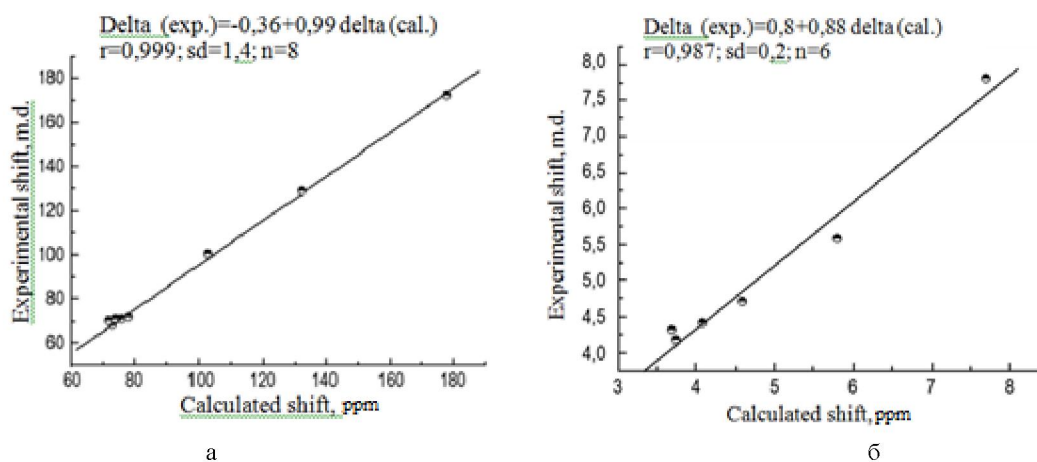
Changing the effective charge on the carbon and hydrogen atoms in the ligands affects the chemical shifts in the NMR spectroscopy.

Table. 4 shows the experimental [9] and calculated in Gaussian's program chemical shifts such ligands as cyclopentadienyl and benzene in the free state and in complexes with iron (ferrocene and ferrocene carboxylic acid).

Table 4 – The chemical shifts in the NMR spectrum

Molecule	Experimental Shift ¹³ C	Calculated Shift ¹³ C	Experimental Shift ¹ H	Calculated Shift ¹ H
Cyclopentadienyl anion	100	103,2; 103,0; 102,9	5,57	5,7; 5,8; 6,0
Ferrocene	67,85	72,6; 73,1	4,15	3,66; 3,76; 3,81
ferrocene carboxylic acid	171,9; 71,7; 70,9; 69,8; 69,4	178; 78; 76; 74; 72	12,2; 4,7; 4,4; 4,3	4,6; 4,1; 3,7
Benzene	128,5	132,6	7,8	7,7
Cr(Bz) ₂		80,2; 79,4; 80,5		4,1; 4,2; 4,3

It can be seen that the interaction of the organic ligand with a metal ion leads to significant reductions of the shear of carbon atoms and protons, while the difference between the experimental and calculated values are close to each other (Fig. 3). Such changes of the chemical shifts associated with a shift of the electron density from carbon and hydrogen atoms.

Figure 3 – The relation between the experimental and calculated chemical shifts in the NMR spectra of (a - ¹³C, b - ¹H)

Comparison of the IR spectra

Using an optimized geometry, we calculated IR spectrum of ferrocene. Most of the 57 frequencies

have zero or very low intensity in the spectrum do not appear. All are grouped into five peaks, since some frequencies are very close and merge on the spectrum. Fig. 4 shows calculated IR spectrum of ferrocene with five peaks clearly visible, which agrees well with the experimental spectrum (Fig. 5).

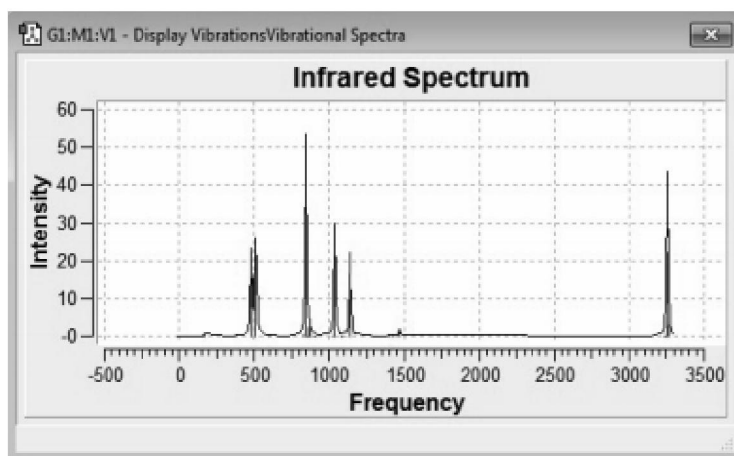


Figure 4 – Calculated by B3LYP / 6-31G * IR ferrocene, cm^{-1}

With Gaussian Viewer program we conducted a frequency assignment. All results are presented in Table. 5.

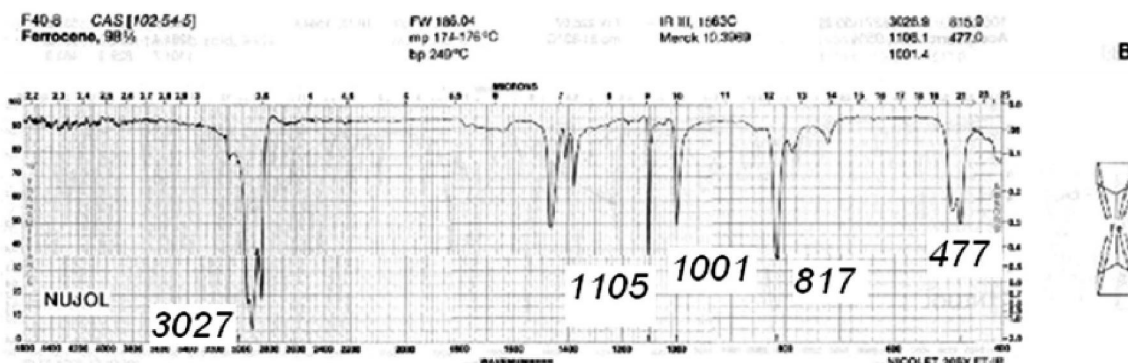


Figure 5 – Experimental IR ferrocene (nonlinear range) [10]

The first peak $\nu = 477 \text{ cm}^{-1}$ corresponds to the movement of the iron atom on the symmetry axis between rings. Close there to peak $\nu = 511 \text{ cm}^{-1}$ corresponds to the movement of the iron atom in a plane parallel to the rings. In the experimental spectrum are two peaks in this area with a maximum at 477 cm^{-1} . In the IR spectrum dibenzenechromium these vibration frequencies are 452 and 488 cm^{-1} .

In forming a complex of ferrocene in the cyclopentadienyl fragments only two frequencies are reduced - breathing vibration of the ring and valence vibration of C-C bonds at 17 and 32 cm^{-1} , respectively. Decreasing of the frequency corresponding to the bond, indicating it's weakening and increases its length. Indeed, the length carbon-carbon bond increased to $0,014 \text{ \AA}$. It can be assumed that part of the π -electron density shifted to free orbitals of the iron atom. That is realized donor-acceptor ($\text{Fe} \leftarrow \text{C}_2\text{H}_4$) interaction. On the other hand, is not excluded the transfer of the electrons of lone electron pairs of iron atoms to the π^* -orbital of the cyclopentadienyl, which also weakens the C-C bond. For a deeper understanding of the relationship of nature in the metallocene is necessary to analyze the redistribution of electron density the formation of their initial compounds.

Analysis of chemical bonds in the molecules ferrocene and dibenzenechromium

Calculation of natural orbital bonds (NBO) [11] showed that the ferrocene has 3 three-center bonds between carbon and iron: one bonding (Figure 6) and two antibonding. In the formation of bonding

molecular orbitals take part non-hybrid carbon 2p orbitals and the d-orbitals of the iron atom. The occupancy of bonding orbital is 1.5 e, and non-bonding are 1.2 and 0.2 e. It is not difficult to assume that such interactions may be 5 or even 10. And the symmetric geometry indicates the equivalence of these interactions.

All interaction between the orbitals in the framework theory of excitation of second-order can be divided into several groups. The first group is responsible for the donor-acceptor interaction: $\pi(\text{C-C}) \rightarrow \text{LP}, \text{LP}^*(\text{Fe})$. The total energy is equal to the disturbance 331 kcal/mol. Taking into account the three-center bond C-Fe-C donation energy rises to 371 kcal/mol. It is clear that the bond is formed not between concrete atoms ring and iron, and between the π -bond (C=C fragment) and iron atom. Since the Fe-C₂ fragment represents isosceles triangle, then this bond should be regarded as a predominantly three-center.

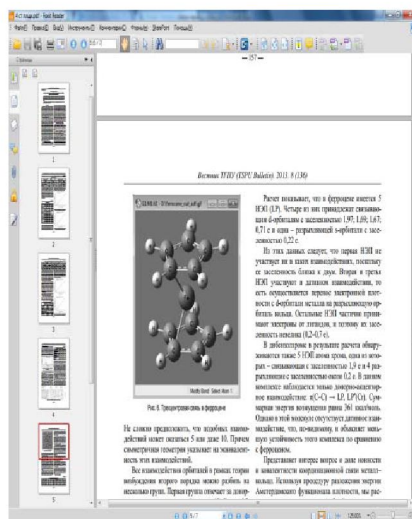


Figure 6 – The three-center bonds in ferrocene

The second group is a dative reacting $\text{LP}(\text{Fe}) \rightarrow \pi^*(\text{C-C})$ with the total perturbation energy 129 kcal/mol, which is about three times less than the donor-acceptor interaction. Thus, the calculation shows that in a molecule of ferrocene dominant interaction exceeds dative.

Our calculations show that in ferrocene are 5 electron lone pairs (LP). Four of them belong to the bonding d-orbitals with occupancy about 1.97; 1.69; 1.67; 0.71 e and one - antibonding s-orbital with occupancy 0.22 e.

From these data it follows that the first LP not involved in any interactions as its occupancy is close to two. The second and third LP involved in dative interaction, that it has carried out the transfer of electron density from the metal d-orbitals to the antibonding orbital. Other LP partially accept electrons from the ligand and therefore their occupancy is small (0.2-0.7 e).

As a result of the calculation dibenzenechromium also found 5 LP of the chromium atom, one of which – bonding with occupancy 1.9 e and 4 non-bonding with occupancy about 0.2 e. This complex shows only the donor-acceptor interaction: $\pi(\text{C-C}) \rightarrow \text{LP}, \text{LP}^*(\text{Cr})$. The total perturbation energy is 361 kcal/mol. However, in this molecule missing dative interaction that appears explains to be less stable this complex the compared to ferrocene.

The question of the proportion of ionic and covalent character and coordination to the metal ring is of interest. Using the procedure of decomposition energy from ADF, we calculated the following contributions (tab. 6).

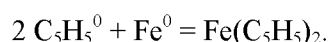
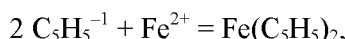
$$E_{\text{tot}} = E_{\text{orb}} + E_{\text{elstat}} + E_{\text{Pauli}},$$

where E_{orb} – energy contribution charge interaction between all the orbitals of the system; E_{Pauli} – the contribution that characterizes the energy of repulsion of fragments; E_{elstat} – an investment that includes the electrostatic attraction of the molecule fragments.

Table 6 – Analysis of the decomposition of the energy, kcal/mol

Energy	Ferrocene	Cp ⁻¹	Fe ²⁺	ΔE	Dibenzolhrom	Benzene	Cr ⁰	ΔE
E _{орб}	-12628	-5896	542	-1388	-15243	-7381	35	-446
E _{эл-стат}	-2817	-1092	0	-633	-3297	-1346	0	-605
E _{Павлнн}	12331	5573	0	1185	14814	6969	0	876
E _{общ}	-3115	-1415	542	-827	-3726	-1758	35	-210

According to the law of Hess, we can calculate the change in the contribution of each energy contribution upon complex formation. This change of the energy will apply to the new bond Fe atom with rings. Scheme ferrocene molecules forming reaction can occur both by ionic and radical mechanisms:



According to the first mechanism from Table 6, orbital energy (covalent bonds) exceeds the electrostatic energy (ionicity of the bond), with the proportion of covalent bond is 69%.

For dibenzenechromium molecules ($2\text{C}_6\text{H}_6 + \text{Cr}^0 = \text{Cr}(\text{C}_6\text{H}_6)_2$) the calculation leads to other relationships between the orbital and covalent interactions. It can be seen that the change in the electrostatic energy is greater than the orbital, and the proportion of covalent bond is only 42%.

Table 7 shows the average energy bonds with the iron atom, taken from the literature.

Table 7 – Average energy values of some chemical bonds with the Fe atom

	E _{average} , kJ/mol
Fe-O	926
Fe-S	797
Fe-C	376

Using the calculated total energy by ionic mechanism, the total energy of all bonds between the cyclopentadienyl rings and an iron atom is 827 kcal/mol (tab. 6). Dividing this value by the number of bonds (provided that all atoms are bonding, they should be ten) we obtain 82.7 kcal/mol or 346 kJ/mol. That is, the bonding energy between each carbon atom and the iron atom is close to the average, which means that all bonds are full. A detailed calculation in program Gaussian over the Gibbs free energy change it gives the value of 703 kcal/mol. In considering of the radical mechanism the ADF program gives the total energy of 232 kcal/mol, and change of the Gibbs free energy was found 199 kcal/mol. These results agree with the experimental values (635 kcal/mol for ionic process and 158 kcal/mol for the radical [12, 13]).

Dibenzenechromium molecule is somewhat less stable. Considering that there exist 12 equal bonds, the bonding energy between chromium and carbon atoms was 73 kJ/mol, which is less energy π-bond.

Conclusions

Optimize the structure a series of metallocenes. It is shown that the ferrocene is symmetry D_{5d} and is located in the eclipsed conformation (gas phase). Similar structures are designed for other metals.

It is shown that the calculated length of metal-carbon bonds and carbon-carbon frequency in the IR spectrum, chemical shifts of ¹H and ¹³C NMR ferrocene and its acid in good agreement with experimental data.

It is shown that for the ferrocene donor-acceptor interaction π(C-C)→LP, LP*(Fe) about three times exceeds the dative interaction LP(Fe)→π*(C-C). For dibenzenechromium chemical bond is described only the donor-acceptor interaction of π(C-C)→LP, LP*(Cr), but dative interaction is absent.

Decomposition of the energy in the complexes of ferrocene and dibenzenechromium showed that the contribution of Fe-C covalent bond is 69%, in Cr-C - 42%. The energy of each of the ten bonds in ferrocene is 346 kJ/mol, and the energy of each of the 12 bonds in dibenzenechromium is 73 kJ/mol, indicating a much lower stability of the complex.

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ТЫҒЫЗДЫҚ ФУНКЦИОНАЛ ТЕОРИЯСЫНЫҢ ӘДІСТЕРІМЕН МЕТАЛЛОЦЕНДЕРДЕГІ ХИМИЯЛЫҚ БАЙЛАНЫСТЫҢ ТАЛДАУЫ

Аннотация. Жұмыста тығыздықтың екі түрлі функционалдарымен металлоцелдер молекулаларының геометриясын оптималдауы жүргізілген. Алынған құрылымдық және спектралды мәліметтер бар тәжірибелік мәндермен салыстырылды. Табиғи валентті орбитальдар тәсілімен есептеу негізінде металлоцелдердің түзілуі кезіндегі донорлы-акцепторлы және дативті әрекеттесулердің шамасы туралы қорытынды жасалды. Энергияның ыдырау жолымен металл және көміртегі атомдар арасындағы иондылық және коваленттілік мәндері алынды.

Түйін сөздер: тығыздық функционалының теориясы, металлоцелдер, донор-акцепторлы және дативті әрекеттесулер, байланыстың коваленттілігі.

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АНАЛИЗ ХИМИЧЕСКОЙ СВЯЗИ В МЕТАЛЛОЦЕНАХ МЕТОДАМИ ТЕОРИИ ФУНКЦИОНАЛА ПЛОТНОСТИ

Аннотация. В работе проведена оптимизация геометрии молекул металлоценов двумя различными функционалами плотности. Полученные структурные и спектральные данные сопоставлены с имеющимися экспериментальными значениями. На основании расчета методом натуральных валентных орбиталей сделан вывод о величине донорно-акцепторного и дативного взаимодействий при образовании металлоценов. С использованием процедуры разложения энергии получены значения ионности и ковалентности связи между атомами металла и углерода.

Ключевые слова: теория функционала плотности, металлоцены, донорно-акцепторное и дативное взаимодействие, ковалентность связи.