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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 D5d 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)		
	$Fe(C_5H_5)_2$	Cp	$Fe(C_5H_5)_2$ S = 0	Cp	$Fe(C_5H_5)_2$ S = 0	$Fe(C_5H_5)_2$ 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
$Pb(C_5H_5)_2$	Pb–C	2,778	2,777	2,770
	C–C	1,430	1,419	1,415
$Sn(C_5H_5)_2$	Sn–C	2,706	2,727	2,646
	C–C	1,431	1,419	1,420
$Be(C_5H_5)_2$	Be–C	1,93	2,05	2,04
	C–C		1,418	1,415
$Ni(C_5H_5)_2$	Ni–C	2,196	2,132	
	C–C	1,430	1,408	
$Co(C_5H_5)_2$	Co–C	2,119	2,130	
	C–C	1,429	1,421	
$Ti(C_5H_5)_2Cl_2$	Ti–C	2,372	2,394	2,384
	C–C	1,397	1,407	1,407
$Mn(C_5H_5)_2$	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.).

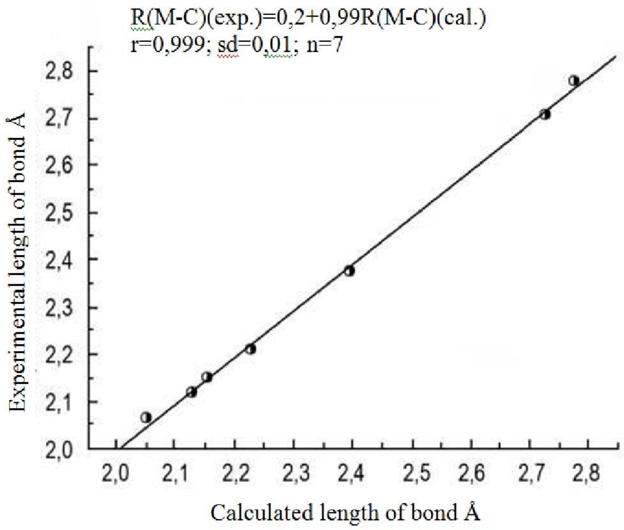

Figure 1 – The relationship between the experimental and calculated by B3LYP/6-31G(d) bond lengths in the metallocene

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.

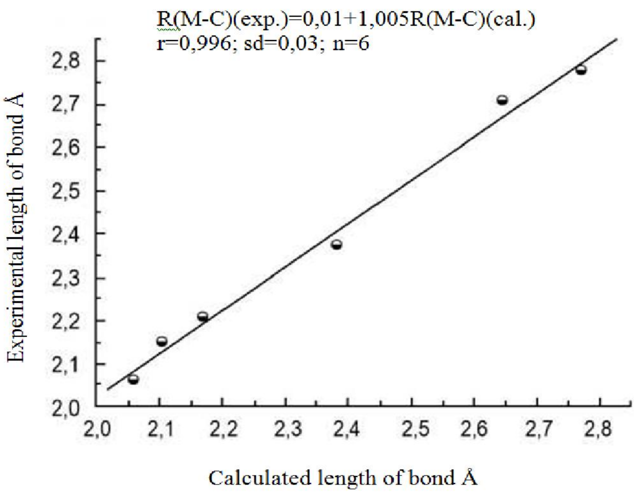

Figure 2 – The relationship between the experimental and calculated by BP86/TZ2P+ bond lengths in the metallocene

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, Hershfild 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.