Nature of Fe—CH$_2$ bonds in ferrocenylmethyl and ferrocenylenedimethyl cations

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Quantum-chemical calculations of ferrocenylmethyl ($[C_5H_5FeC_5H_4CH_2]^+$) and ferrocenylenedimethyl ($[C_5H_5FeC_5H_3(CH_2)_2]^{2+}$) cations with full geometry optimization were carried out using the Hartree—Fock (HF) approximation, density functional theory (DFT), and at the second-order Møller—Plesset (MP2) level of perturbation theory in the 6-311G* basis set. The methods with inclusion of electron correlation in explicit form indicate that the CH$_2$ groups deviate from the cyclopentadienyl ring planes toward the Fe atom due to formation of the Fe—CH$_2$ bonds. According to Hartree—Fock calculations, ligands in these ions are virtually planar. The metallonium character of the ions studied was demonstrated based on the results of analysis of the electron density distribution and frontier orbitals.

Key words: *ab initio* quantum-chemical calculations, Hartree—Fock approximation, density functional theory, Møller—Plesset perturbation theory, ferrocenylmethyl cation, ferrocenylenedimethyl cation, ion structure, nature of chemical bond, role of electron correlation, metallonium bonding.

Recently,[1—8] a number of methods for the synthesis of metallonium monocations, $[C_5Me_5MC_5Me_4CH_2]^+$, and dications, $[C_5Me_5MC_5Me_3(CH_2)_2]^{2+}$ and $M[C_5Me_4(CH_2)]_2^{2+}$, based on permethylmetallocene compounds of iron subgroup elements (M = Fe, Ru, Os) were developed and the cations were synthesized. Monocations with the CH$_2$ groups bent toward the metal atoms were called metallonium monocations.[6] These (rather) stable salts have been structurally characterized[2,3] by X-ray diffraction analysis. Dications are less stable; however, ^{1}H NMR studies showed that they can exist in a solution of the superacid CF$_3$SO$_3$H in the temperature range from −60 to +60 °C.[5]

Interest in theoretical study of the nature of chemical bonding in these ions is due to unusual structure and great potential of these species in the synthesis of novel types of metallocene derivatives. Of particular importance is to investigate the structure of the simplest representative of this class of ions, the ferrocenylmethyl cation, which forms extremely unstable salts that have therefore not been studied by X-ray diffraction analysis. This cation is a key to metallocene chemistry. The structure of this species was the subject of extensive discussions (see Refs. 9 and 10).

The ferrocene molecule was studied by a number of theoretical methods with different basis sets.[11—14] The pioneering quantum-chemical calculations of the $[C_5Me_5FeC_5Me_4CH_2]^+$, $[C_5Me_5FeC_5Me_3(CH_2)_2]^{2+}$,

and $Fe[C_5Me_4(CH_2)]_2^{2+}$ cations and their fragments were carried out by semiempirical methods (EHM and CNDO).[4,5,15] The first nonempirical quantum-chemical study of the metallonium monocations and dications (M = Fe, Ru, Os) in the gas phase were carried out by the DFT/BLYP/LanL2DZ method.[16] The geometric parameters of $[C_5Me_5MC_5Me_4CH_2]^+$ monocations were shown to agree with the results of X-ray diffraction studies. The computational method employed reproduced well all geometric parameters except for the M—CH$_2$ interatomic distances (they are most sensitive to changes in the phase states) and the angles between the M—CH$_2$ bond and the plane of the cyclopentadienyl ligand (α). The calculated relative stabilities of the monocations and dications containing various M atoms (Fe < Ru < Os) are also in agreement with the data of mass spectrometric studies.[16]

In this work we present the results of high-level quantum-chemical calculations of the monocation $[C_5H_5FeC_5H_4(CH_2)]^+$ (**1**) and dication $[C_5H_5FeC_5H_3(CH_2)_2]^{2+}$ (**2**) carried out to elucidate the nature of chemical bonding in metallonium ions. To the best of our knowledge, no quantum-chemical studies of these species have been reported so far.

Calculation Procedure

Calculations of cations **1** and **2** in the gas-phase will full geometry optimization were carried out using the Hartree—Fock

[†] Deceased.

(HF) method and the density functional approach with the Becke—Lee—Yang—Parr functional (DFT/BLYP)[17,18] and at the second-order Møller—Plesset level (MP2) of perturbation theory with the 6-311G* basis set. Though the accuracy of DFT/BLYP calculations of the atomization energies is somewhat lower compared to that obtained from B3LYP calculations (see Ref. 19), we rejected the hybrid DFT approach since in this case the exchange and correlation energies are functions of the electron density. Calculations were carried out on CRAY J-90 (National Energy Research Supercomputer Center, Berkeley, California, USA) and SGI Power Challenge Computer Servers (Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratories, Richland, Washington, USA) supercomputers using the GAUSSIAN-98 program suite.[20]

Results and Discussion

The geometries of monocation **1** and dication **2** were optimized using the parameters of the eclipsed (energetically more stable) conformation of the ferrocene molecule in the gas phase[21] as initial approximation.

The atomic numbering scheme for the iron monocation and dication in question is given below.

1   **2**
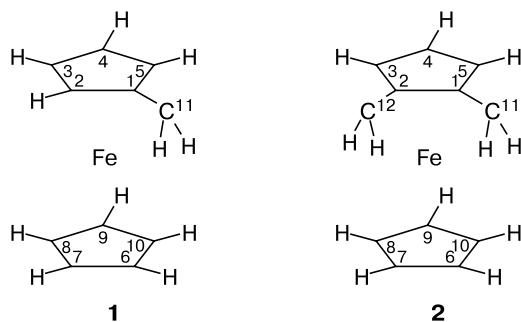
Hydrogen atoms have the same numbers as the C atoms to which they are bonded. Pairs of H atoms at the C(11) and C(12) atoms are denoted H(11), H(11´) and H(12), H(12´), respectively. The primed H atoms are separated by a shorter distance (this holds only for structure **2**).

Table 1 presents the results of our calculations of cations **1** and **2** in the gas phase, namely, the total energies, principal interatomic distances, and the angles α, β, γ, δ, and ε. Notations of the angles are as follows: the angles between the C(11)—C(1) or C(12)—C(2) bonds and the plane of the C(1)...C(5) five-membered ring are denoted α; the H(11´)—C(11)—C(1)—H(11) and H(12)—C(12)—C(2)—H(12´) dihedral angles are denoted β (they characterize the deviation of the H(11) and H(11´) atoms from the plane of the C(1)=C(11) "double" bond and of the H(12) and H(12´) atoms from the plane of the C(2)=C(12) "double" bond, respectively); the H(11´)—C(11)—H(11) and H(12)—C(12)—H(12´) angles are denoted γ; the H(11)—C(11)—C(1) and H(12)—C(12)—C(2) angles are denoted δ, and the

H(11´)—C(11)—C(1), H(12´)—C(12)—C(2) angles are denoted $\delta´$.

Since no experimental data are available for cations **1** and **2** studied in this work, comparison with particular experimental parameters is merely a convention. In addition, one should keep in mind that the experimental data were obtained for the solid phase, whereas our calculations were performed for species in the gas phase. Therefore, the main goal is to compare the results obtained by different computational methods.

According to HF calculations of monocation **1**, the CH₂ group lies virtually in the C(1)...C(5) carbon ring plane (the angle α is 4.4°). The Fe—C(k) distances ($k = 1$—5) are close (on the average, 2.35 Å), while the average distance from the Fe atom to the C atoms of the second cyclopentadienyl ring is 2.20 Å. Both these values are somewhat larger than the Fe—C bond lengths in the free ferrocene molecule (2.03 Å).[23] The C(1)—C(11) distance in monocation **1** is 1.338 Å and equals the carbon-carbon bond length in the ethylene molecule (1.337 Å).[23] The Fe—C(11) distance is very long (3.176 Å). Hartree—Fock calculations gave a pronounced alternation of the C—C bond lengths in the PhCH₂ fragment, which is characteristic of the fulvene ligand. Thus, in the HF approximation monocation **1** can be treated as an iron complex with the fulvene and cyclopentadienyl ligands.

Quite different results were obtained for monocation **1** by the DFT/BLYP method. The angle α is 37.5°, which means that the C(1)—C(11) bond is strongly bent toward the Fe atom. Among all Fe—C bonds in this system, the Fe—C(1) distance (1.985 Å) is the shortest. The Fe—C(11) separation in monocation **1** is 2.283 Å, while the C(1)—C(11) bond length is 1.404 Å. Different results obtained by different methods can suggest coexistence of two structures of the monocation, namely, a fulvene (planar) and a metallonium (nonplanar) structure. Therefore, we performed additional calculations using the geometry obtained from DFT/BLYP calculations as initial approximation for the HF optimization. However, we again obtained a planar C₅H₄CH₂ fragment. Similarly, DFT/BLYP calculations with the starting geometric parameters corresponding to the energy minimum for HF calculations led to nonplanar structure of monocation **1**.

Even larger values of the angle α and longer C(1)—C(11) distances in monocation **1** were obtained by the MP2 method (see Table 1). The C(11)—C(1)—C(2) angle appreciably decreases and approaches the tetrahedral angle.

Similar changes were also observed for dication **2** on going from HF to the DFT/BLYP and MP2 methods. According to HF calculations, the C₅H₃(CH₂)₂ ligand is planar, whereas the methods with inclusion of electron correlation (DFT/BLYP, MP2) give substantial bending

Table 1. Geometric parameters and total energies (E_{tot}) of monocation **1** and dication **2** obtained from HF, DFT/BLYP, and MP2 calculations

Parameter	**1**			**2**		
	HF	DFT/BLYP*	MP2	HF	DFT/BLYP	MP2
Bond length/Å						
Fe—C(1)	2.343	1.985 (1.968)	1.832	2.564	2.014	1.833
Fe—C(2)	2.348	2.089 (2.050)	1.928	2.564	2.014	1.833
Fe—C(3)	2.364	2.162 (2.116)	1.984	2.612	2.181	1.989
Fe—C(4)	2.364	2.162 (2.136)	1.984	2.597	2.290	1.962
Fe—C(5)	2.348	2.089 (2.054)	1.928	2.612	2.181	1.989
Fe—C(6)	2.211	2.130 (2.094)	1.994	2.177	2.157	2.063
Fe—C(7)	2.187	2.114 (2.104)	1.978	2.177	2.157	2.063
Fe—C(8)	2.213	2.089 (2.055)	1.933	1.152	2.117	1.986
Fe—C(9)	2.213	2.089 (2.010)	1.933	2.195	2.106	1.930
Fe—C(10)	2.187	2.114 (2.122)	1.978	2.152	2.117	1.986
Fe—C(11)	3.176	2.283 (2.567)	1.989	3.432	2.422	1.987
Fe—C(12)	—	—	—	3.432	2.422	1.987
C(1)—C(2)	1.476	1.471 (1.449)	1.437	1.494	1.499	1.441
C(2)—C(3)	1.350	1.416 (1.378)	1.457	1.437	1.456	1.424
C(3)—C(4)	1.473	1.443 (1.457)	1.423	1.395	1.420	1.471
C(4)—C(5)	1.350	1.416 (1.419)	1.457	1.395	1.420	1.471
C(1)—C(5)	1.476	1.471 (1.416)	1.437	1.436	1.456	1.424
C(6)—C(7)	1.407	1.436 (1.431)	1.440	1.393	1.437	1.449
C(7)—C(8)	1.425	1.433 (1.370)	1.424	1.431	1.437	1.420
C(8)—C(9)	1.394	1.442 (1.400)	1.467	1.407	1.438	1.477
C(9)—C(10)	1.425	1.433 (1.410)	1.424	1.407	1.438	1.477
C(6)—C(10)	1.407	1.436 (1.430)	1.440	1.431	1.437	1.420
C(1)—C(11)	1.338	1.404 (1.370)	1.474	1.352	1.396	1.473
C(2)—C(12)	—	—	—	1.352	1.396	1.473
Bond angle/deg						
α	4.4	37.5 (23.6)	51.2	−2.7	32.4	52.8
β	179.0	161.0	132.5	180.0	165.8	130.4
γ	117.0	116.6	112.8	116.4	116.3	110.3
δ	121.5	120.4	114.5	120.9	120.0	112.8
δ′	121.5	120.4	114.5	122.7	122.3	117.8
ε	127.1	118.0	110.8	130.3	121.1	110.2
−E/au	1685.0127	1689.2068	1686.9038	1723.0394	1727.4784	1725.1218

* The interatomic distances in the crystal of monocation [C$_5$Me$_5$FeC$_5$Me$_4$CH$_2$]$^+$, obtained in X-ray diffraction study,[22] are given in parentheses.

of the CH$_2$ groups toward the Fe atom (α = 32.4 and 52.8° for the DFT/BLYP and MP2 calculations, respectively).

The Mulliken effective charges on the Fe atom and CH$_2$ groups in cations **1** and **2** calculated by the HF and DFT/BLYP (MP2) methods are also appreciably different. The inclusion of electron correlation causes a decrease in the charge on the Fe atom by ~0.5e and in the net effective charge on the CH$_2$ group by 0.3e (Table 2). Thus, from the standpoint of the effective charges these ions are treated as carbocationic centers (HF approximation) or as metallonium ions (DFT/BLYP and MP2 methods).

Scheme 1 presents the Cartesian axes of reference for cation **1**. The *y* axis passes through the Fe atom and the
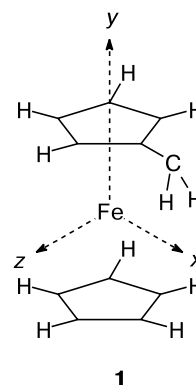
Scheme 1

1

Table 2. Effective atomic charges (q/au) obtained from HF, DFT/BLYP, and MP2 calculations of monocation **1** and dication **2**

Atom	HF		DFT/BLYP		MP2	
	1	**2**	**1**	**2**	**1**	**2**
Fe	1.382	1.384	0.880	0.870	0.858	0.695
C(1)	−0.161	−0.267	0.044	0.043	−0.029	0.039
C(2)	−0.332	−0.267	−0.268	0.043	−0.287	0.039
C(3)	−0.246	−0.013	−0.215	−0.230	−0.251	−0.137
C(4)	−0.246	−0.382	−0.215	−0.144	−0.251	−0.312
C(5)	−0.332	−0.013	−0.268	−0.230	−0.287	−0.137
C(6)	−0.232	−0.307	−0.213	−0.191	−0.295	−0.175
C(7)	−0.460	−0.307	−0.245	−0.191	−0.258	−0.175
C(8)	−0.312	−0.505	−0.230	−0.218	−0.275	−0.230
C(9)	−0.312	−0.170	−0.230	−0.188	−0.275	−0.287
C(10)	−0.460	−0.505	−0.245	−0.218	−0.258	−0.230
C(11)	−0.259	−0.204	−0.481	−0.440	−0.478	−0.534
C(12)	—	−0.204	—	−0.440	—	−0.534
H(2)	0.278	—	0.240	—	0.277	—
H(3)	0.285	0.342	0.241	0.293	0.283	0.330
H(4)	0.285	0.333	0.241	0.295	0.283	0.346
H(5)	0.278	0.342	0.240	0.293	0.277	0.330
H(6)	0.246	0.273	0.245	0.287	0.290	0.333
H(7)	0.247	0.273	0.235	0.287	0.271	0.333
H(8)	0.248	0.276	0.235	0.284	0.276	0.319
H(9)	0.248	0.274	0.235	0.283	0.276	0.351
H(10)	0.247	0.276	0.235	0.284	0.271	0.319
H(11)	0.303	0.350	0.265	0.312	0.292	0.340
H(11′)	0.303	0.336	0.265	0.305	0.292	0.317
H(12)	—	0.350	—	0.312	—	0.340
H(12′)	—	0.336	—	0.305	—	0.317

center of the upper five-membered cycle, the origin coincides with the position of the Fe atom, the x axis lies in the plane passing through the Fe, C(1), and C(11) atoms, and the z axis is perpendicular to the x and y axes.

Analysis of the MOs of monocation **1** according to the Hartree—Fock theory shows that the highest occupied MO (HOMO, $E = -0.47068$ au) is nearly pure π-orbital of the cyclopentadienyl ring with very small contribution of the Fe AOs. The filled MO with somewhat lower energy ($E = -0.47355$ au) also has the π-character and is localized on the cyclopentadienyl ring. The lowest unoccupied MO (LUMO) of monocation **1** ($E = -0.13391$ au) has the π-character; however, it is localized on the fulvene fragment of the monocation. The LUMO has a contribution of the Fe s-AOs.

Analysis of the MOs of monocation **1** in the framework of density functional approach using the coordinates shown in Scheme 1 reveals that the HOMO ($E = -0.34239$ au) is a linear combination of the Fe $4p_z$- and $3d_{yz}$-AOs and of the $2p_z$-orbital of the C(11) atom (this orbital has the π-character toward the interaction between the Fe atom and CH_2 group). The filled MO with somewhat lower energy ($E = -0.34628$ au) has

the σ-character, since the major contribution to this orbital comes from the Fe $3d_{z^2}$- and $3d_{x^2-y^2}$-AOs and the 2s-, $2p_x$-, and $2p_y$-orbitals of the C(11) atom. The orbitals of the Fe and C(11) atoms also make nearly the same contribution to the LUMO of monocation **1** ($E = -0.25917$ au). From these data it follows that the donor-acceptor Fe—CH_2 bond occurs by π-donation and σ-acceptance of an electron. For dication **2** the HF and DFT calculations also give different descriptions of the frontier orbitals.

Only the DFT/BLYP and MP2 methods that include the energy of electron correlation in explicit form can correctly describe the cations under study as metallonium structures. This is in excellent agreement with the results of X-ray diffraction and ^{1}H NMR studies of related permethylated mono-, di-, and trications,[16,22,24] whereas the HF method treats these species as carbocations with planar ligands. From this it follows that nonplanar structure of these ions is mainly due to the effects of electron correlation. To assess the magnitude of these effects, we performed DFT/BLYP calculations of a number of systems with constant geometric parameters. These were the structures **1a** (monocation **1** with the geometric parameters corresponding to the energy minimum according to HF calculations), **1b** (free $C_5H_4CH_2$ ligand with planar structure), and **1c** (nonplanar $C_5H_4CH_2$ ligand with the structure analogous to that of monocation **1**). The total energy difference, $\Delta E = E(\mathbf{1c}) - E(\mathbf{1b}) = 9.7$ kcal mol^{-1}, nearly equals the energy of delocalization of a π-electron to the C(11)—C(1) bond. The energy gain due to passage from planar to nonplanar structure of the monocation is provided by the total energy difference, $\Delta E' = E(\mathbf{1a}) - E(\mathbf{1}) = 28.9$ kcal mol^{-1}. Thus, the energy of the donor-acceptor Fe—CH_2 interaction is 28.9 kcal mol^{-1}, which is much larger than the decrease in the delocalization energy of π-electron of the ligand (9.7 kcal mol^{-1}). According to DFT/BLYP calculations, the difference $\Delta E' - \Delta E$ is 19.2 kcal mol^{-1}.

MP2 calculations give close values of theoretical estimates. The energy gain, $\Delta E' - \Delta E$, due to bending of the CH_2 group toward the Fe atom is 22.2 kcal mol^{-1} larger than the loss of delocalization energy.

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