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ELECTRON STRUCTURE AND CHEMICAL PROPERTIES OF ARENE-CYCLOPENTADIENYLIRON DERIVATIVES

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Summary

The unrestricted Hartry-Fock method in the INDO approximation with modified parametrization is used to study the electron structure of the arene-cyclopentadienyliron cation $[(C_6H_6)Fe(C_5H_5)]^+$ and its derivatives (carbon acids and amines) and also analogous derivatives of ferrocene. The charge distribution among the rings is shown to be unsymmetrical which is manifested in the difference of acidic and basic properties of the rings, confirmed by both direct calculations of acidic dissociation energy and also by experimental observation.

The experimental and theoretical study of the physical properties of sandwich compounds is a comparatively novel and intensively developing field of chemistry, the main attention being paid to symmetrical sandwich structures. Quite a number of quantum chemical calculations has been carried out for such compounds (see, e.g., ref. 1) which identify the character of their electron structure. Unsymmetrical sandwiches are less studied theoretically (ref. 2 is the only paper available); at the same time, chemical properties of mixed arene-cyclopentadienyliron complexes have been thoroughly investigated and an appreciable difference in the behaviour of the 5- and 6-member cycles of these complexes has been demonstrated [3—5]. The aim of the present work is to study the electron structure of such compounds and thus to interprete the existing experimental regularities.

The calculations were carried out by the unrestricted Hartry-Fock method in the INDO approximation. To increase the convergence, we used a special technique of level shifts [6] modified for the unrestricted Hartry-Fock method. This technique proved to be necessary to reach the convergence of energies for some sandwich structures (e.g., $Fe(C_5H_5)_2$) which could be ensured by neither the common procedure, nor the Hartry damping. The level shift parameter ψ for virtual orbits differed from that reported in ref. 7 and varied within 100 to

20 eV for a non-consistent run (1—4th iteration). In the course of attaining the self-consistency, it reduced to 10—2 eV. For open shells this parameter was set equal to zero. Concrete values of the level shift parameter were chosen to ensure maximum convergence rates.

The above method was employed for calculations on the arene-cyclopentadienyliron cation and its derivatives: the acids $[(C_5H_4COOH)Fe(C_6H_6)]^+$ and $[(C_6H_5COOH)Fe(C_5H_5)]^+$, the amines $[(C_5H_4NH_2)Fe(C_6H_6)]^+$ and $[(C_6H_5NH_2)Fe(C_5H_5)]^+$ and the deprotonated acids and protonated amines. Analogous ferrocene derivatives and also free benzoic acid and aniline were calculated for comparison. The parametrization for the metals was as given in ref. 8, that for ring atoms as in ref. 9. We set the distance Fe—C equal to 2.056 Å [10]; the geometry of free benzoic acid and aniline was used for the carboxyl and amino groups of the sandwich acids and amines. The model calculated included 3*d* and 4*s* orbits of the metal and all the valency orbitals of the rings. The proton abstraction (attachment) energy was calculated as the difference between the total energies of the deprotonated (protonated) and primary complexes, as in ref. 11. The geometry distortions caused by deprotonation (protonation) were neglected.

Results

The ground state of the cation $[(C_6H_6)Fe(C_5H_5)]^+$ as well as of the symmetrical sandwiches $[Fe(C_6H_6)_2]^{2+}$ and $Fe(C_5H_5)_2$ is a singlet which is calculated to be 0.8 and 2.0 eV lower than the first excited triplet state for r(Fe—C) = 2.14 Å and 2.056 Å respectively. The calculated ring rotation barrier of the complex is small (<1 kcal/mol). Table 1 lists the upper levels of the MO scheme for the ground state of $[(C_6H_6)Fe(C_5H_5)]^+$ cation at r(Fe—C) 2.14 Å and 2.056 Å. The system possesses only C_s symmetry, however its energy levels are almost degenerate in pairs. It is interesting to note that the higher occupied MOs have no admixture of benzoic ring AOs but consist mainly of metal *d*-orbitals and a linear combination of cyclopentadienyl ring π-orbitals which

TABLE 1

HIGHEST POPULATED MO LEVELS OF THE GROUND STATE FOR THE CATION $[(C_6H_6)Fe(C_5H_5)]^+$

r(Fe—C) (Å)	No.	ϵ (eV)	Type of symmetry	Basic contributions to MO [a]
2.14	1	—16.4572	A''	$0.3(3d_{xz}) + 0.2(4p_x) + 0.8\pi_1^{(5)}$
	2	—16.4575	A'	$0.3(3d_{yz}) + 0.2(4p_y) + 0.8\pi_2^{(5)}$
	3	—17.6125	A'	$0.97(3d_{z^2})$
	4	—17.6903	A'	$0.95(3d_{x^2-y^2})$
	5	—17.6904	A''	$0.95(3d_{xy})$
2.056	1	—16.9654	A''	$0.3(3d_{xy} - 3d_{xz}) + 0.8\pi_1^{(5)}$
	2	—16.9655	A'	$0.3(3d_{x^2-y^2} + 3d_{yz}) + 0.8\pi_2^{(5)}$
	3	—16.9977	A'	$0.85(3d_{x^2-y^2})$
	4	—16.9978	A''	$0.85(3d_{xy})$
	5	—17.0376	A'	$0.96(3d_{x^2})$

[a] $\pi_1^{(5)}$ is the linear combination of corresponding symmetry of cyclopentadienyl ring *p*-orbits.

TABLE 2

CHARGE DENSITY DISTRIBUTION IN ARENECYCLOPENTADIENYLIRON CATION

Fe	C_6H_6			C_5H_5		
q	$q(\Sigma)$	$q(C)$	$q(H)$	$q(\Sigma)$	$q(C)$	$q(H)$
+0.232	+0.654	+0.074	+0.035	+0.114	+0.011	+0.005

agrees with the published calculations [2]. The orbitals $3(A')$, $4(A'')$, $5(A')$, consisting mainly of metal *d*-orbits, have close energy values (especially for r(Fe—C) 2.056 Å), their order changing with r(Fe—C).

For the first excited triplet states the spin populations are calculated to be $\rho(C^{2s}) = 0.00121$ (0.00066); $\rho(H) = 0.0051$ (0.0024) for the cyclopentadienyl ring and $\rho(C^{2s}) = 0.0013$ (0.0007); $\rho(H) = 0.0063$ (0.0028) for the arene ring (values for the cation with r(Fe—C) 2.14 Å in parentheses). Note that in the case of chromocene, r(Cr—C) 2.14 Å, we obtained $\rho(C^{2s}) = -0.0008$ and $\rho(H) = 0.0042$ which is a good fit to experiment (—0.0007 and 0.0049).

Table 2 lists the calculated charge density distribution among the atoms for the cation $[(C_6H_6)Fe(C_5H_5)]^+$. The cation charge is distributed unsymmetrically, the greater positive charge belonging to the arene ring. For comparison with experimental values of pK_a [3—5], we have calculated the protonation and deprotonation energies in sandwich acids and amines (their values are given in Table 3).

Fig. 1a depicts the correlation $\Delta E^g/pK_a$ for the sandwich acids where ΔE^g is the deprotonation energy of a sandwich acid in the gas phase. Fig. 1b shows an analogous correlation diagram for $\Delta E^g/pK_a$ of sandwich amines. Here ΔE^g is the protonation energy of amines in the gas phase. A good correlation between ΔE^g and pK_a is observed in both cases.

According to our calculations, some 75% of the negative charge is accumulated at the —C(OO) group of deprotonated sandwich acid anions and some 72% of the positive charge at the $-NH_3$ group of protonated amine cations. Neglecting the charge delocalization and taking the radii of the COO^- and NH_3^+ groups from ref. 12 we calculated, by the Born formula, the variation of the complex solvation energy at H^+ abstraction (attachment). Fig. 2 presents the

TABLE 3

CALCULATED CHARGES OF HYDROGEN ATOMS

Compound	No.	q_H
$(C_5H_5)Fe(C_5H_4COOH)$	1	0.1636
C_6H_5COOH	2	0.1691
$[(C_6H_6)Fe(C_5H_4COOH)]^+$	3	0.1656
$[(C_5H_5)Fe(C_6H_5COOH)]^+$	4	0.1730
$(C_5H_5)Fe(C_5H_4NH_2)$	5	0.1789
$C_6H_5NH_2$	6	0.1892
$[(C_6H_6)Fe(C_5H_4NH_2)]^+$	7	0.1816
$[(C_5H_5)Fe(C_6H_5NH_2)]^+$	8	0.2198

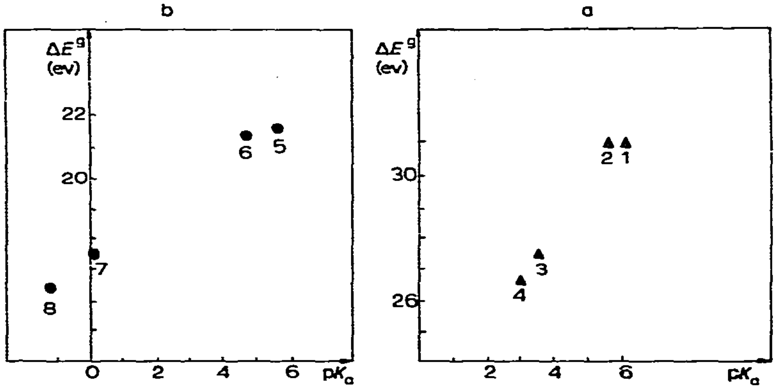

Fig. 1. (a) Correlation diagram $\Delta E^g/pK_a$ for sandwich acids (b) Correlation diagram $\Delta E^g/pK_a$ for sandwich amines (Point numeration as given in Table 3).

general correlation diagram $\Delta E^1/pK_a$ for sandwich acids and amines where ΔE^1 is deprotonation energy in liquids. Thus, taking account of solvation, even in such a simple form, results in the general correlation $\Delta E^1/pK_a$.

The protonation and deprotonation energies calculated by the INDO method are thus seen to reflect fairly well the acid-base properties of arene and cyclopentadienyl carbon acids and amines of the sandwich type complexes. However, use of ΔE as an acidity factor demands some cumbersome calculations. The calculated charge at the hydrogen atom abstracted cannot serve as an acidity factor either since it is seen from Table 3 to correlate neither with ΔE nor pK_a (unlike the case of simple carbon acids calculated in ref. 13).

It appeared that in this case the charge on the ring in the non-substituted sandwich structure can surve as a qualitative characteristic. Table 4 compares calculated charges of the ring denoted by an asterisk, and experimental data on acidity, basicity and chlorine lability in corresponding sandwich derivatives. Acidic properties and chlorine lability in the ring are seen to increase (while the basic properties to decrease) with growing positive charge of the ring. For

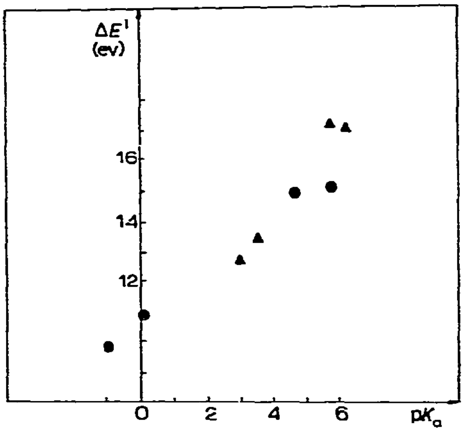

Fig. 2. Correlation diagram $\Delta E^1/pK_a$.

TABLE 4

CALCULATED CHARGES OF THE RINGS OF THE COMPLEXES AND EXPERIMENTAL DATA ON ACIDITY, BASICITY AND CHLORINE LABILITY

	P of ring	pK_a [3] RC*COOH	pK_a [4] RC*NH$_2$	Relative Cl lability in RC*Cl [5]
$(C_5H_5)Fe(C_5H_5)^*$	−0.070	6.11	5.76	—
C_6H_6	0.000	5.64	4.58	10^{-9} [a]
$[(C_6H_6)Fe(C_5H_5)^*]^+$	0.114	3.53	0.20	10^{-5}
$[(C_6H_6)^*Fe(C_5H_5)]^+$	0.654	3.05	−1.07	10^{-2}

[a] Data for nNO$_2$-C$_6$H$_4$Cl.

instance, chloro-ferrocene ($q < 0$) is unable of non-catalytic nucleophilic substitution, while the chlorine lability in arene-cyclopentadienyliron ring (q_{max}) is comparable with that of 2,4-dinitrochlorobenzene [5].

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