

ANALYSIS OF ^1H NMR DATA FOR ARENE-METAL COMPLEXES USING EXTENDED HÜCKEL CALCULATIONS

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This work reports the use of extended Hückel molecular orbital (EHMO) calculations to correlate p_z electronic densities of aromatic carbons in group VI metal-bis(η^6 -arene) complexes with the respective ^1H NMR chemical shifts. The effect of delocalization on the acceptor properties and stabilization of ligand orbitals is analyzed comparing complexes of naphthalene, biphenyle and fluorene.

Key words: Organometallics; Sandwich complexes; η^6 -Arene complexes; EHC method, NMR spectroscopy.

^1H NMR chemical shifts in aromatic molecules depend not only on the diamagnetic shielding effect of s electrons which surround the nucleus but also on magnetic fields generated by electrons moving around the molecule. The second effect is called a "ring current". This electron motion produces a magnetic field that "deshields" the protons in the plane of the aromatic ring, that is, moves the corresponding peaks to higher chemical shift values¹. Since the s , p_x and p_y electrons are mainly involved in the σ system, the p_z electrons should be responsible for this ring current. Both these effects are strongly dependent on the inductive characteristics of the substituents present in the molecule. However, due to large differences in chemical shifts between aromatic and non-aromatic molecules, it is possible that the ring current effect will be the most important in aromatic molecules.

Interpretation of NMR spectra of aromatic molecules is largely reported in the literature, but most often it is the ^{13}C NMR that is studied, due to larger chemical shifts range. Initially the spectra were analyzed in terms of substituents effects, correlating chemical shifts with Taft σ constants². Unsuccessful application of this correlation to other nuclei like ^{19}F forced the authors to use more complex approaches, like the Karplus and Pople formalism³ and derivatives⁴, which also include the effect of electron circulations. If the molecules studied are metal complexes, it is necessary to take into account also the effects of the metal-ligand interaction on the electron densities⁵⁻⁷.

An easy way of calculating the π -electron densities of an aromatic molecule is the extended Hückel molecular orbital (EHMO) calculations. Therefore, in this work,

correlations between ^1H NMR chemical shifts of organometallic complexes with aromatic ligands and p_z electronic densities are tested in order to verify the importance of ring currents. The results obtained using this method include the effects of substituents, ligand–metal bonding and metal–ligand backbonding.

EXPERIMENTAL

Method

All the ^1H NMR data were obtained on deuterated benzene solutions from MVS (Metal Vapour Synthesis) synthesized sandwich-type organometallic complexes described in the literature^{8–12}.

Computational Details

All the extended Hückel¹³ calculations were made with CACAO (Computer Aided Composition of Atomic Orbitals)¹⁴ with modified H_{ij} (ref.¹⁵). The basis set for the metal atoms consisted of ns , $n\eta$ and $(n - 1)d$ orbitals. The s and p orbitals were described by single Slater type wave functions, and d orbitals were taken as contracted linear combinations of two Slater-type wave functions. The six-membered rings were considered as regular 140 pm side hexagons; 108 pm was used for all the C–H distances.

Since the orbital populations are sensitive to the choice of structural parameters, in particular for the metal–arene bond length, all the extended Hückel MO calculations were carried out on a model complex of fixed geometry, in order to isolate the effect of the substituent on the ring carbons p_z orbital populations. The model, shown in Fig. 1, was built from the data collected in the Cambridge Structural Database¹⁶. The two arene rings were kept in an eclipsed conformation and, when a substituent replaced a hydrogen of the ring, an overall C_s symmetry was used. For $L = \text{CF}_3$, a C_2 overall symmetry was used, due to stereochemical reasons.

RESULTS AND DISCUSSION

Preliminary calculations carried out on bis(η^6 -fluorene) organometallic sandwich-type complexes have shown a linear dependence between the ^1H NMR chemical shift and the p_z orbital population in the Cr, Mo and W complexes, increasing in the same order⁸ (Fig. 2).

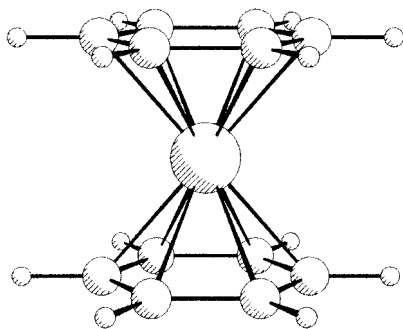


FIG. 1

Model complex for all EHMO calculations: M–L (centroid) = 161 pm, C–C = 140 pm, C–H = 108 pm, C–Me = 155 pm, C–F = 125 pm, C–Cl = 165 pm, C–CF₃ = 145 pm, C–OMe = 138 pm, OMe = 138 pm, C–C–F = 110°, C–O–Me = 110°

We tried to generalize this trend to other bis-arene sandwich-type systems, changing simultaneously the metal centre and substituting one hydrogen in each benzene ring by various substituents, spanning different electronic characteristics. The results of these calculations also produced a linear dependence, depicted in Fig. 3, between chemical shifts of ortho protons and p_z orbital populations (meta and para chemical shifts, as well as p_z densities are almost unaffected by the substitution).

The analysis of Fig. 2 shows that almost all chromium and tungsten values are below the line while all the molybdenum values are above. This behaviour can be explained

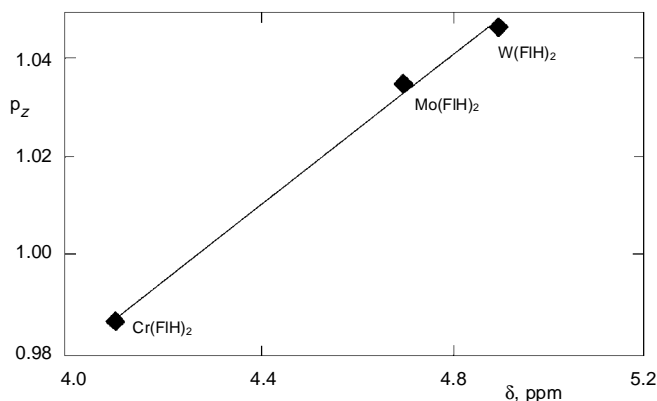


FIG. 2

p_z Orbital populations (p_z meta hydrogens) vs ^1H NMR chemical shifts (δ) in $\text{M}(\text{FIH})_2$ complexes ($y = 0.0752x + 0.6793$, $R^2 = 0.996$)

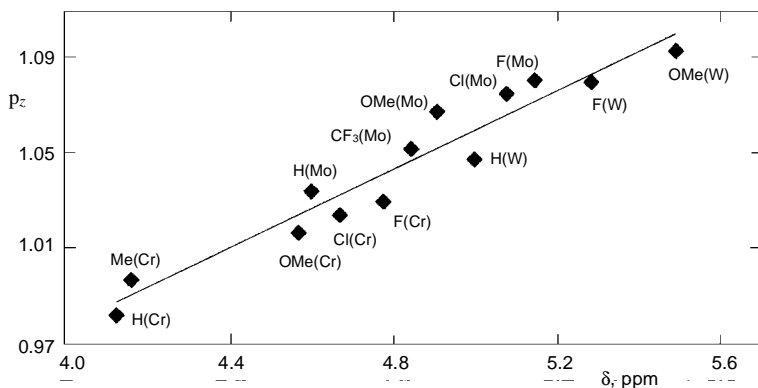


FIG. 3

Correlation between orbital populations (p_z) and chemical shifts (δ) ($y = 0.0809x + 0.6536$, $R^2 = 0.996$)

by the rigidity of the adopted model: relaxation of the metal–ligand bond lengths to appropriate values for each metal will move the points towards the correlation line. Another immediate conclusion from this picture is that the chromium complexes are on the lower side of the correlation, corresponding to more shielded protons, while Mo and W complexes span over the upper side of the trend line. This feature is understandable when considering the relative energies of the metal d electrons, which increase from

TABLE I
FMO analysis for the interaction between the $(C_6H_6)_2$ and metal centre

Parameter	Cr	Mo	W
Overlap populations, e			
HOMO $(C_6H_6)_2/d(M)$ π bonding interaction	0.31	0.31	0.31
LUMO $(C_6H_6)_2/d(M)$ π backbonding interaction	0.28	0.36	0.39
Energies, eV			
d (M)	-11.22	-10.50	-10.37
HOMO $(C_6H_6)_2$	-12.49	-12.49	-12.49
LUMO $(C_6H_6)_2$	-8.61	-8.61	-8.61
HOMO $M(C_6H_6)_2$	-10.64	-9.64	-9.29
SHOMO $M(C_6H_6)_2$ π backbonding interaction	-11.59	-11.21	-11.16
THOMO $M(C_6H_6)_2$ π bonding interaction	-13.18	-13.10	-13.08
LUMO $M(C_6H_6)_2$	-8.06	-8.06	-8.06

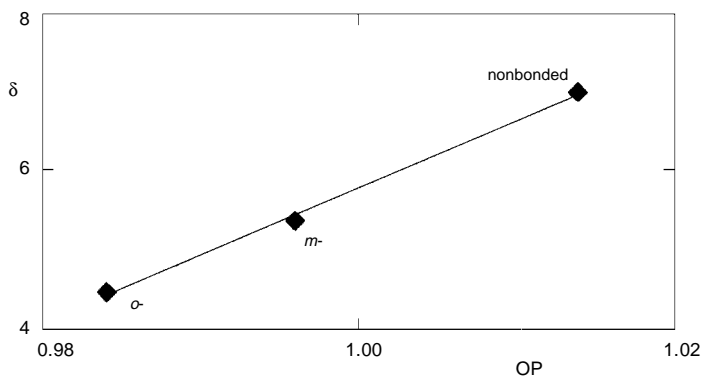


FIG. 4
 p_z Orbital populations (OP) vs 1H NMR chemical shifts (δ) in $Cr(naph)_2$ complex (ortho and meta positions are referred to the common C–C bond) ($y = 83.07x - 77.277$, $R^2 = 0.998$)

chromium to tungsten, enhancing the π backbonding and weakening the π bonding in the same order (Table I).

The ^1H NMR data for fused aromatic systems like naphthalene and biphenyle, or other polycyclic aromatic compounds like fluorene, can also be rationalized in terms of the charge densities in p_z orbitals, but eventually extended to the protons of the non-bonded rings. Figure 4 shows an example of this type of correlation for $\text{Cr}(\text{naphthalene})_2$, where the protons of the uncoordinated ring were also included.

As seen in Figs 2 and 3, these correlations remain valid for other group VI metals, but, unfortunately, no data are available for the tungsten compound because, to our best knowledge, it has not been synthesized yet. Nevertheless, EHMO calculations show a good internal correlation for molybdenum complexes, where 4 different peaks were detected in the ^1H NMR corresponding to the calculated 4 different p_z electronic densities (Fig. 5) as opposed to the chromium complexes, where only three NMR peaks and electronic densities were observed.

Extending further the aromatic systems to biphenylene, we obtained the electronic populations shown in Table II, but the NMR data are available only for the chromium complex. The synthetic difficulties with the Mo and particularly with W complexes

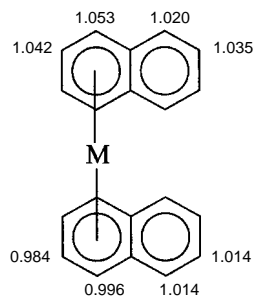
TABLE II

p_z Orbital populations for $\text{M}(\text{biphenylene})_2$ complexes. ^1H NMR chemical shifts (δ , ppm) are given in parentheses, when available

Compound	<i>o</i> -	<i>m</i> -	<i>o</i> -(nb) ^a	<i>m</i> -(nb) ^a
$\text{Cr}(\text{biphenylene})_2$	1.009 (4.37)	0.989 (4.21)	1.049 (6.56)	1.023 (6.30)
$\text{Mo}(\text{biphenylene})_2$	1.058	1.038	1.067	1.036
$\text{W}(\text{biphenylene})_2$	1.072	1.086	1.080	1.086

^a Nonbonded ring.

FIG. 5
 p_z Charge densities for bis-naphthalene complexes of Cr and Mo (M = Mo upper ring; M = Cr lower ring)



may arise from the fact that the HOMO/LUMO gap tends to vanish in the latter, leading to a Jahn–Teller distortion that may be stereochemically unfavourable.

CONCLUSIONS

The correlations reported in this work between carbon p_z electronic densities and ^1H NMR chemical shifts demonstrate the importance of ring currents in the NMR spectra of aromatic organometallic complexes. The p_z electronic densities are influenced by the inductive characteristics of the substituents present in the rings, by the bonding and backbonding properties of the metal–ligand bond and by the extension of the aromatic system. The present method proves to be an easy way of interpreting and predicting ^1H NMR chemical shifts for aromatic organometallic complexes.

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