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Electronic analysis of vanadium and iron complexes containing distorted aromatic rings

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Abstract Aromatic rings can suffer severe distortions upon substituting transition metal centers with certain kinds of organometallic compounds. This property is very interesting because aromaticity can remain despite the deformation. Theoretical calculations at the density functional theory level were carried out on two such structures containing vanadium and iron centres $[(C_5H_5\text{-}V\text{-}H)_2C_6H_6$ and $(CpFe)_2 C_6(CH_3)_6]$ in order to analyze the nature of the bonds as well as the magnitude of the prevalent aromaticity and how this depends on the electronic characteristics around each metal atom. The analysis of aromaticity was carried out on the basis of known methods, such as HOMA and FLU, with consistent results. The results also show features that suggest a possible catalytic behavior of the species under study.

Keywords Aromaticity · Density functional calculation · Conformational flexibility · Organometallic complex

Introduction

Some material compounds derived from organometallic complexes have been studied in order to correlate their molecular structure and electronic properties with their intrinsic characteristics [1]. One type of molecular structure that has

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been the object of several studies and much interest is the multiple decker sandwich complex [2]. These complexes have been synthesised by various methods and with different transition metals. In our case, interest is focused on some previously prepared [3] complexes containing vanadium and similar iron complexes [4] (Fig. 1).
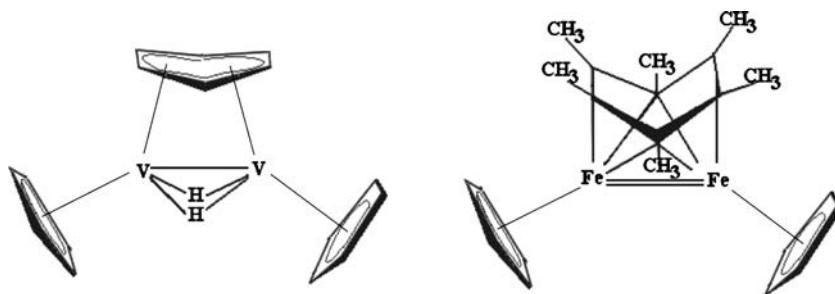
These kinds of compound present a collection of peculiar characteristics; all the ring carbon atoms of the arene are bonded to an M_2 unit that can be bridged by other ligands. Different cases exist, one of which is when M_2 is di-vanadium, in which case the fold-angle is approximately 20° and all the C–C distances within the benzene ring are equal (1.43 Å), as shown in the schematic perspective in Fig. 2. The other case is when M_2 is di-iron (Fig. 3), where the ligand angle is much more pronounced (dihedral angle 43°). In this molecule, the C–C double bond that is coordinated to only one iron atom is significantly shorter than the other C–C bond in the ligand. This causes two different situations: the first, for the case of the di-vanadium complex, results in a structural arrangement that yields two similar but slightly different organic fragments in such a way that an aromatic benzene is formed, whereas a localized dienediyl structure is formed for the di-iron complex case [5].

A theoretical study of complex $(C_5H_5\text{–}V\text{–}H)_2C_6H_6$ was carried out by Bènard and coworkers [6]. Here, the authors presented an orbital interaction diagram among the metal d orbitals of the Cp–V dimmer, π level of benzene and σ and σ* of H_2. Their results indicated molecular stability due to the metal–metal and metal–ligand interactions. Additional considerations that arise from other studies of the electronic configurations of d electrons conclude that the energy gap between singlet and triplet states is small, indicating that direct electronic interactions involved in this mechanism are the factors responsible for stabilization of the whole system [6].

The molecules $(C_5H_5–V–H)_2C_6H_6$ and $(CpFe)_2C_6R_6$ contain distorted aromatic rings that remain stable in spite of the distortion. Solà et. al. [7], studied the influence of out-of-plane and in-plane deformations on the aromaticity of the benzene by different aromaticity indices. These studies indicated a minor loss of aromaticity for the boat-like out-of-plane deformation.

The aromaticity concept [8] is considered when a molecule is a planar monocyclic hydrocarbon with delocalization (4n+2) π-electrons in isolated rings, and there are several methods to measure these properties [9]. There is an interesting collection of studies that relate the different properties of aromatic molecules with intrinsic aromaticity, yielding indices that can be compared with a standard model (benzene in most cases). These nature of these indices differs depending on the property considered.

Different features and manifestation are usually used to analyze aromatic compounds. Aromaticity is evaluated by classical structural and electronic methods. There are several methods based in molecular geometry, with the best performance obtained with the harmonic oscillator measure of aromaticity (HOMA) [10, 11]; this is the method employed in the present work. Other aromaticity criteria are based on electron delocalization and take into account the mobility of electrons; this is the case with the para-delocalization index (PDI) [12] and fluctuation index (FLU) [13], which describe the fluctuation of electronic charge between adjacent atoms in a given ring. These three indices were used to calculate aromaticity in the molecules under study.

The main goal of this paper is to explain what happens to the electronic structure and molecular geometry when a synthesized molecule has distortions. Good examples are the organometallic compounds mentioned above. It has been proposed that the benzene ring of the vanadium complex remains aromatic whereas that of the iron complex adopts an "ylure"-like configuration, both being stable. In this study, the aromaticity of both structures was evaluated with different methods. The organometallic compounds chosen have molecular structures that contain a bimetallic triple-decker with a polycyclic system. These kinds of compounds can be useful as catalytic agents due to their electronic properties. The purpose of the study is to establish the source of the large stability of these species in spite of their strong deformations and their fluxional behavior.

Methods

The electronic structure of organometallic compounds is commonly studied from first principles, using methods that include electronic correlation and spin-orbital corrections. In the present study, the density functional theory [14] (DFT) included in the Gaussian03 software [15] was used. A pure DFT method, containing Becke's gradient correc-
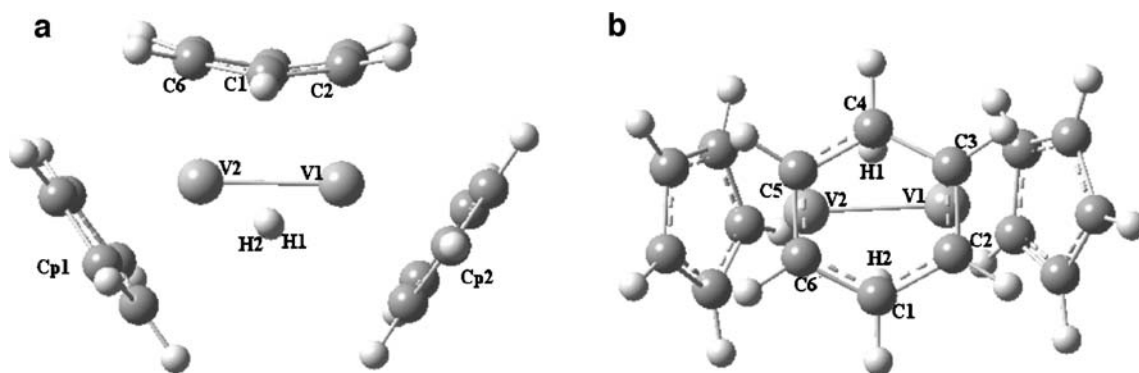

Fig. 2 Shape of the stable organometallic molecule $(C_5H_5–V–H)_2C_6H_6$ obtained by the geometry optimization calculation. **a** Front view of the molecule showing the distorted ring. **b** Upper view of the molecule
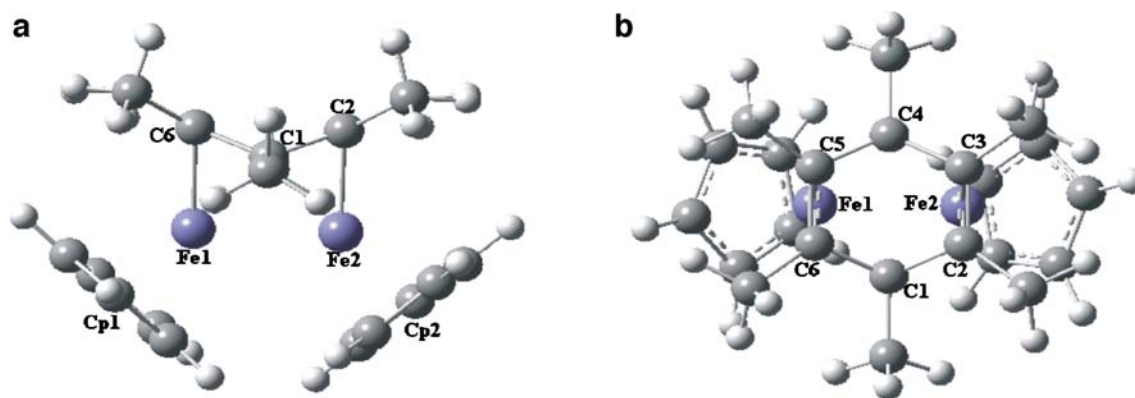
Fig. 3 The geometry optimization calculation of the molecule $(C_5H_5-Fe)_2C_6(CH_3)_6$ showing the atom positions. **a** Front view of the molecule showing the distorted ring. **b** Upper view of the molecule. Note that C6, C1, C2 form an angle preserving the symmetry, this angle is more open in this case (with respect to the aromatic plane) than the compound of vanadium

tion for exchange [16] and Perdew-Wang's for correlation [17], and B3LYP methods were used for geometry optimization. In the case of the B3LYP functional, the non-local correlation was provided by the LYP expression and the correction was carried out by means of the VWN functional. The 6-311++g(d,p) basis set was used in all calculations for light atoms. This computational level has shown good results for geometric optimization of molecules that contain two or three metal-complex fragments bond to arenes as ligands [18, 19]. In the case of transition metal atoms, the LAN2DZ pseudo potential was used for V and Fe. The aromaticity indices, HOMA, PDI and FLU were calculated. The benzene molecule was used as a reference for these aromaticity indices.

Results and discussion

The optimized geometry of the molecular structure of $(C_5H_5-V-H)_2C_6H_6$ is shown in Figs. 1 and 2. This struc-

ture has a bi-vanadium (III) unit with bridged bonds to the hydrogen atoms. The vanadium (III) are π-bonded to Cp fragments and deformed benzene. There is no bond between the hydrogen atoms that are perpendicular to the V–V bond. The molecule belongs to the C_{2v} group; bond lengths are given in Table 1.

The iron complex under study seems to be similar to that of vanadium due to the distorted benzene ring; however, it is very different. In the case of the iron complex, the C–C distances on the benzene ring show a lack of symmetry and there is a straight metal–metal double bond. This feature confers very different characteristics to this compound that are described by the calculations. Figure 1 shows both of the optimized structures. In fact the presence of the Cp fragments and the benzene ring suggest that this is a family of compounds; however, this is not true, indeed this figure shows the large deformation of the iron complex. The optimized structure of the iron compound alone is shown in Fig. 3.

Mulliken population analysis shows that the vanadium and hydrogen atoms are positively charged, with 0.13e and

Table 1 Bond length atoms and angles of two organometallic compounds, obtained by density functional theory (DFT) calculation and X-ray data [2] only for $(C_5H_5-V-H)_2C_6H_6$

$(C_5H_5-V-H)_2C_6H_6$,			$(C_5H_5-Fe)_2C_6(CH_3)_6$	
Bond length (atom)	Experimental (Å)	Calculated (Å)	Bond length (atom)	Calculated (Å)
V1-V2	2.425	2.310	Fe1-Fe2	2.470
H1-H2	1.970	2.220	C- CH$_3$	1.500
V1-C2	2.143	2.180	Fe2-C2	2.010
V1-C3	2.159	2.090	Fe2-C3	2.010
V2-H1	1.690	1.750	Fe1-C1	2.260
V1-H2	1.700	1.770	Fe2-C4	2.260
V1-Cp	2.287	2.338	Fe1-Cp	2.154
C-C	1.427	1.430	C-C	1.425
Angle (atom)	Experimental (degrees)	Calculated (degrees)	Angle (atom)	Calculated (degrees)
C6-C1-C2	116.8	122.9	C6-C1-C2	114.1

These values show the average C–C bond of the benzene molecule and the Cp link to metal

0.08e, while the Cps and benzene ring are negatively charged, at −0.11e and −0.21e, respectively. In other words, the vanadium atoms donate charge to the rings such that there is a positive core and a surrounding negative shell. The molecule as a whole is neutral.

The distortion of benzene has been extensively studied; the strain energy of the structural geometry is in equilibrium between σ-resistance to distortion and π-distortional [20] contributions. In our case, the distortion in the organometallic compound is due to the presence of the vanadium atoms. One empty orbital of vanadium interacts with four carbon atoms of the benzene ring that have π-electron delocalization as a part of its framework, and gives place to a coordinated bond with the vanadium atom as was previously described [6]. The vanadium–benzene bond generates a distortion in the structural geometry [2]. In this distortion, the benzene ring adopts a winged configuration forming two faces separated by an axis of symmetry over the carbon atoms (C1, C4). The distortion generated by the empty orbitals of the vanadium atoms has an effect on the carbon atoms (C1–C2–C3–C4) in one wing, whereas in the other face the orbitals of the other vanadium atom generate a similar effect with the corresponding set of carbon atoms (C1–C4–C5–C6), yielding strain but a symmetrical conformation.

The other molecular structure studied is $(C_5H_5-Fe)_2C_6(CH_3)_6$. This structure has two iron atoms joined to Cp fragments, and the $C_6(CH_3)_6$ is deformed as shown in Fig. 3. In this molecule, the normal π-bonding with the expected bond length to the Cp fragment is present. However, there is an unusual π-bond between the iron atom and the distorted aromatic ring; this last bond seems to be very localized, suggesting the ring is no longer aromatic. All bond lengths are shown in Table 1. The reported limits for bond length changes in deformed benzene that retains its aromatic stabilization is 0.3 to −0.3 Å [21].

Mulliken population analysis shows that the Fe atom has a charge of 0.19e, whereas the Cp fragment joined to the iron has a total charge of −0.075e, an expected result considering the ionic interaction between Fe and Cp [22]. The most important point is found in the interaction between the deformed aromatic ring and the iron atoms because the ring has −0.22e of charge. This suggests that the carbon atoms that support the bond with each iron atom

have an excess of charge. This fact in turn implies electronic localization—an argument that reinforces the idea that the aromaticity in the ring is broken. Therefore, the distortion of the benzene ring destroys the aromaticity.

The main discussion about the deformation of these rings is based on the use of aromaticity indices. The calculation of aromaticity indices allows analysis of several factors related to the intrinsic aromaticity and geometry changes (HOMA), energy changes (ASE) [23], magnetic properties (NICS) [24] and electronic and structural features (PDI and FLU). In the present case, the chosen aromaticity indices were HOMA, PDI and FLU since all of these are useful in evaluating the consequences of the loss of aromaticity due to changes in the structure of the ring. These indices were calculated for the two compounds; the first for the organometallic compound of vanadium, in which the aromaticity apparently remains, and the second for the iron complex, in which the aromaticity is apparently broken. The values are given in Table 2.

The HOMA index of the distorted benzene ring of both molecules yields the first interesting results. In the case of $(C_5H_5-V-H)_2C_6H_6$, the value obtained was 0.766 whereas in the case of $(C_5H_5-Fe)_2C_6(CH_3)_6$, the result was 0.313. These values indicate a loss of aromaticity due to changes in the torsion angle caused by symmetry change. The iron complex has a very low value of aromaticity, whereas for the vanadium complex the effect is a small reduction. The relationship between the torsion angle and the aromaticity is direct. The value of the torsion angle for the iron complex is 33° whereas for the vanadium complex it is 29°. Obviously, the severe deformation in the former case causes a separation of the molecular orbitals that supports electronic delocalization, resulting in a loss of aromaticity. This effect is not so important in the case of vanadium and the electronic delocalization remains.

The PDI index was used to calculate aromaticity in the aromatic rings of both organometallic compounds. The first organometallic compound with a distorted benzene ring that contains vanadium atoms presents a value of 0.0193 for this index, whereas in the case of the iron compound the same index value is 0.0327. Benzene has a PDI of 0.103 and $C_6(CH_3)_6$ of 0.089. This indicates that there is loss of aromaticity for the two organometallic compounds due to the distortion of the rings of both molecules, but that the vanadium compound is less aromatic than the iron one.

Table 2 B3LYP/6311-G++(p,d) HOMA, PDI (electron) and FLU for the organometallic compound $(C_5H_5-V-H)_2C_6H_6$, and $(C_5H_5-Fe)_2C_6(CH_3)_6$, obtained of calculation using DFT. *HOMA* Harmonic oscillator measure of aromaticity, *PDI* para-delocalization index, *FLU* fluctuation index

Aromaticity index	$(C_5H_5-V-H)_2C_6H_6$	$(C_5H_5-Fe)_2C_6(CH_3)_6$	Benzene	$C_6(CH_3)_6$
HOMA	0.7662	0.3134	0.999	0.9993
PDI	0.0193	0.0327	0.103	0.0892
FLU	0.0190	0.0429	0.000	0.0014
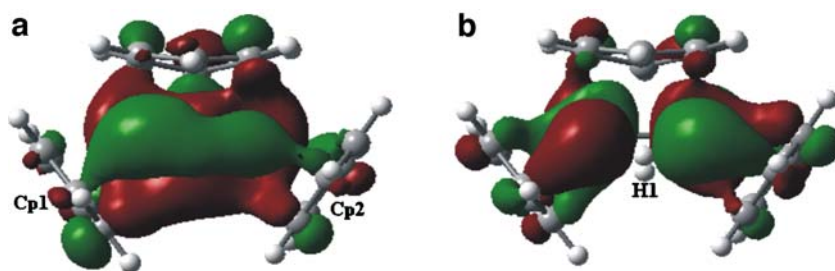
Nevertheless, this latter index of aromaticity exhibits a weakness with regard to the same measure carried out by means of the HOMA and FLU indices. A difference with the PDI index is that, like HOMA, it provides a local criterion [25]. Thus, Fradera and Bader [26, 27] claim that the information supplied by an index of delocalization is independent of any association with bonding among the atoms implied; therefore, the only factor that has influence in this particular index is the intrinsic distortion. and this is the reason why this index seems to give the opposite results with respect to the other two indices, which quantify distortion by taking the ideal situation of a very symmetrical structure (generally benzene) as a reference.

The FLU index represents the other measure of aromaticity for the ring [28]. In this case, the same behavior was observed for both compounds; there was a reduction of aromatic character due to the effect of distortion on the benzene ring. The value for the vanadium molecule was 0.0190, whereas for the iron molecule it was 0.0429, the value for benzene is 0.0 and that of $C_6(CH_3)_6$ is 0.0014. These values indicate a reduction in the aromatic character but the order of these results is similar to that seen for the HOMA index, i.e., the vanadium compound retains a little aromaticity, but the iron compound is almost non-aromatic. These results are very important because they indicate that the first compound should have a strong delocalization in the region that includes all the aromatic rings and the metallic center, whereas in the second case the double bonds on the distorted benzene ring should be strictly localized. Obviously, the chemical behavior of the two molecules should be very different.

On the other hand, a corresponding analysis of the frontier molecular orbitals for both structures was performed; Bènard and coworkers [6] performed a similar analysis taking advantage of the Extended Hückel calculations. Our results are somewhat different than those found in that work but the interaction seems to be similar. The molecule belongs to the C_{2v} group, the shapes of the frontier molecular orbital of $(C_5H_5–V–H)_2C_6H_6$ are shown in Fig. 4. These results show that the orbital distribution corresponds to the b_1 irreducible representation for the case of the HOMO, and the molecular orbital is focused mainly in a small region of the vanadium atom and practically all of the atomic contribution of the hydrogen atoms. Comparing with the LUMO, the irreducible representation now corresponds mainly to the π bond between the Cp rings and the metal atoms, and belongs to the b_2 irreducible representation. The main feature to note, which is also the main difference from the analysis by Bènard et al. [6], is that the HOMO distribution shows a strong character of a banana bond. This indicates that the first electrons that can be donated should correspond to the hydrogen atoms, and therefore the molecule should react through hydrogen bridges; this is the reason why this material has been suggested as a source of molecular hydrogen, justifying its use as a possible material for hydrogen storage.

The shapes of the frontier orbital for the iron complex are shown in Fig. 5. The molecule also corresponds to the
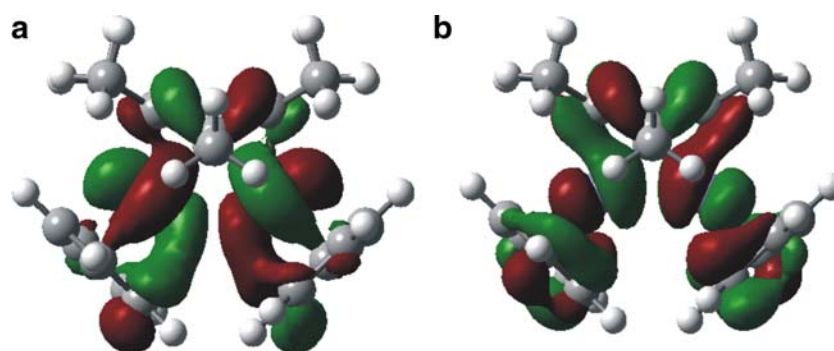

Fig. 5 Shape of the frontier molecular orbitals of the iron complex. a The HOMO has contributions mainly from the Cp rings and the localized double bonds of benzene. b The LUMO has a similar contribution to the HOMO but is focused in the internal bonds of the aromatic rings and distorted benzene

C_{2v} symmetry group. Both orbitals have a similar contribution: the HOMO belongs to the b_1 irreducible representation whereas LUMO belongs to the b_2. The HOMO has a mainly π bond character and is localized in the interactions among the aromatic Cp rings and the localized double bonds of the distorted benzene ring. The LUMO is similar but the tendency is more localized on the σ bonds on the ligands, with little contribution of these bonds to the link with the metal atoms.

Conclusions

The study of the distortion in the aromatic rings of these molecules through aromaticity indices and frontier molecular orbitals analysis indicates that the main cause of the deformation is due to interaction with metal atoms. The calculations of the aromaticity indices for the two molecules showing this kind of distortion indicates that there is loss of aromaticity in both cases, as demonstrated by similar tendencies seen in HOMA and FLU results. However, the lack of aromaticity is stronger in the case of the iron compound, where the double bonds are completely localized indicating a total loss of aromaticity, whereas in the case of the vanadium complex the lack of aromaticity is only partial; this feature allows the molecule to exhibit the observed fluxional isomerism. Frontier orbital analysis clearly shows that the vanadium complex could be a good candidate for application as a hydrogen storage material.

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