ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 603 (2000) 225–234

Journal of Organo metallic Chemistry

Manganese (I) complexes of *p*-xylene and [2*n*] cyclophanes from a theoretical sight

Roberto Salcedo *, Luis E. Sansores, Ana Martínez, Larissa Alexandrova, Montserrat García

Instituto de Investigaciónes en Materiales, Universidad Nacional Autonoma de Mexico, Ciudad Universitaria, Circuito Exterior, A.P. 70-360, Delegación de Coyoacán, 04510 Mexico D.F., Mexico

Received 9 December 1999; received in revised form 11 March 2000

Abstract

Theoretical B3LYP/6-311G** calculations were performed in order to understand the electronic structure and the structural behavior of bis(*p*-xylene) and bis([2,2]-*p*-cyclophane) manganese (I) complexes. The minimum energy configuration of bis-(*p*-xylene) has D_{2d} symmetry while that of bis([2,2]-*p*-cyclophane) has D_2 symmetry. The energy difference between the D_{2d} and the D_{2h} structures for both compounds is small. The results of the calculation for the pseudorotational barrier indicate that a process of interconversion may be possible. A comparison between experimental and theoretical infrared spectra was done for bis(*p*-xylene) Mn(I). Theoretical and experimental spectra are in good agreement. For both compounds, the HOMO has a big contribution from the metal orbital. In bis([2,2]-*p*-cyclophane) manganese (I) the HOMO and HOMO-1 form a bridge between the rings, this can explain some of the electric flow. Much of the evidences that we present in this work, indicates that transannular electronic interaction for bis([2,2]-*p*-cyclophane) manganese (I) is present. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Manganese (I); *p*-Xylene; [2*n*] cyclophanes; Molecular orbital

1. Introduction

Electrically conductive polymers are of significant practical value. In order to obtain the desired electrical or magnetic properties, it is important to realize synthetic theoretical design of the candidate material. An outstanding characteristic of [2*n*] cyclophanes, as revealed from photoelectron and ESR studies, is the interaction of the two aromatic decks to give an overall π-electron system [1–3]. This feature has fomented the research on [2*n*] cyclophanes metal complexes, searching for polymers made from monomers through transition metal complexation that show this type of delocalization [4]. One of the goals has been to examine whether this delocalization can be extended through transition-metal complexation [5–8]. If so, a polymer can be envisioned which should show interesting electrical properties and possibly conductivity.

The synthesis of a polymer in which the monomer unit is a transition-metal complex of a cyclophane is feasible. One of the advantages of transition-metal–cyclophane complexes is that the individual metal atoms can have different formal oxidation states. This condition can provide the electron holes necessary for a conduction band and the polymer could be a unidimensional electrical conductor [9]. Reports of the formation of oligomeric products where the monomer unit is arene–transition metal sandwich complexes have been already published [10]. Since bis(*p*-xylene) and bis(2,2-*p*-cyclophane) sandwich complexes with transition metals were demonstrated to have very similar characteristics [11], we have studied the structural behavior of these manganese (I) complexes in the same theoretical fashion.

Metal cyclophane complexes have been studied for many years [12]. There are several reports of the synthesis and properties of Ru [5,8,9,13–21], Cr [11,22,23], Fe [24–32] and Co [33–38] cyclophanes. Furthermore, since the discovery of ferrocene [39], the interest in arene-complexes has increased, as is evidenced by some review articles [40].

* Corresponding author. Fax: +52-5-6161201.
E-mail address: salcedo@servidor.unam.mx (R. Salcedo)

0022-328X/00/$ - see front matter © 2000 Published by Elsevier Science S.A. All rights reserved.
PII: S0022-328X(00)00184-4

The reaction of transition metal vapors with arene substrates is a well-established route to a host of bis(arene)metal sandwich complexes, some of which are difficult or impossible to prepare by more conventional methods [41,42]. However, manganese appears to be an exception as there are few references to manganese atom chemistry and low yields are generally found in reactions which lead to organomanganese products [43]. The bis(arene)manganese cations have been isolated as their salts, but the neutral form has not been observed. Stable $(\sigma^6\text{-}C_6H_6)_2Mn^+$ has not been isolated and no IR-spectra of this kind of complexes has been reported. The only experimental spectra results are from the Mn–*p*-xylylene system [44]. The cocondensated mixture of *p*-xylylene and Mn vapors (the content of Mn was about 30%) on a 80 K cooled substrate was irradiated by UV-light from a mercury lamp to produce poly-*p*-xylylene–Mn system without heating. The IR-spectra of the original and polymerized systems were measured at 80 K to avoid destruction of the Mn complexes. Since the chemical structure of units of poly-*p*-xylylene are very similar to *p*-xylene, the results of the theoretical simulation of the interaction between Mn and *p*-xylene can be applied to understand the experimental observations of the Mn–poly-*p*-xylylene system.

The electronic characteristics of manganese have precluded the preparation of metal arene complexes. Only manganese ions can allow agreement with the effective atomic number rule (18 electron rule). Hence, an adequate cation of manganese can follow this rule and be considered a possibility, further more manganocene and some of its derivatives are known as non-stable molecules [45] but the synthesis of diphenyl manganese has not been reported.

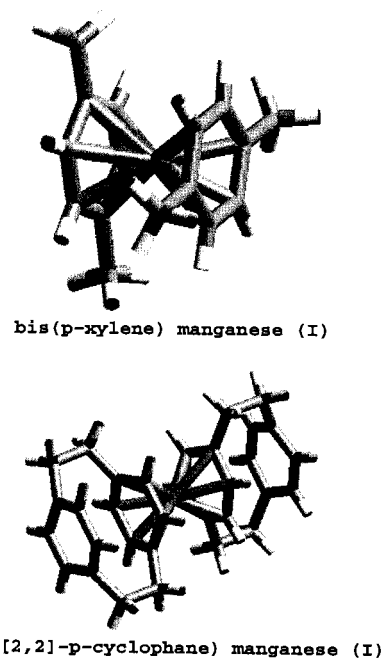


Fig. 1. Optimized geometries of bis(*p*-xylene) manganese (I) and bis([2,2]-*p*-cyclophane manganese (I). Both molecules are cations with a positive charge (+1) and follow the 18-electron rule.

Our earlier experimental results [44] indicate that manganese can be used in the reaction with *p*-xylene and [2*n*] cyclophanes. In this paper, we present a theoretical study of the manganese (I) complexes of *p*-xylene and [2*n*] cyclophanes (Fig. 1).

The aim is two-folded, on one hand, to help understand and identify the compound associated with the experimental results [44]. Based on our results, we can predict the macromolecular characteristics of bis([2,2]-*p*-cyclophane) manganese (I) on the basis of its electronic behavior. It is important to emphasize that these are the first arene–Mn complexes of this kind that are reported and that there is no description of them in the literature. The present study is important since we present the main characteristics of these new molecules from a theoretical point of view. We present optimized geometries, Infrared spectra, molecular orbitals pictures, Mülliken charge analysis and electronic density for manganese (I) complexes of *p*-xylene and [2*n*] cyclophanes. The behavior of both compounds is analyzed suggesting a transannular electronic interaction for bis([2,2]-*p*-cyclophane) manganese (I).

2. Computational details

Geometry optimizations were done at B3LYP/6-311G** level, starting with a bent structure and without any symmetry restrictions. To discriminate between minima from other critical points on the potential energy surface, frequency calculations were performed at the same level of theory. All the calculations were performed using the Gaussian 94 code [46].

3. Results and discussion

The optimized geometries of bis(*p*-xylene) manganese (I) and bis([2,2]-*p*-cyclophane) manganese (I) are presented in Fig. 1. Both molecules are cations with a positive (+1) charge and follow the eighteen electrons rule. For bis(*p*-xylene) manganese (I), the molecule belongs to the D_{2d} point group Tables 2a,b and 3a–c. The methyl substituents are rotated in such a way that the rings takeon a staggered conformation. The rings are very regular, almost flat, the torsion angle is 4.6°, bond lengths are only 0.005 Å different from one another and the bond angles are distorted by 2.5 and 1.7° from the sp^2 bond. For each ring there are four carbons at 2.145 Å from the manganese and two at 2.176 Å. This regularity of the rings indicates that there

Table 1
Mülliken charge analysis for both compounds

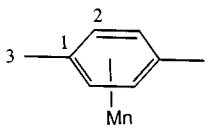
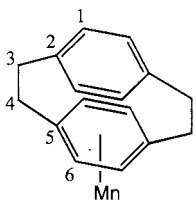
Structure	Atom	D_{2d} Charge	D_{2h} Charge
	C1	−0.191	−0.188
	C2	−0.109	−0.113
	H2	0.127	0.125
	C3	−0.227	−0.226
	H3	0.164	0.166
	H3	0.127	0.127
	H3	0.127	0.127
	Mn	0.860	0.876
	C1	−0.068	−0.068
	H1	−0.097	−0.097
	C2	0.094	0.095
	C3	−0.172	−0.172
	H3	0.139	0.139
	H3	0.139	0.139
	C4	−0.153	−0.153
	H4	0.134	0.134
	H4	0.134	0.134
	C5	−0.130	−0.135
	C6	−0.131	−0.128
	H6	0.113	0.111
	Mn	0.921	0.926

Table 2a
Bond lengths and angles for bis(p-xylene) manganese (I) in the D_{2d} configuration Fig. 10

Bond length (Å)		Angle (°)	
C1–C2	1.415	C7–C1–C2	121.3
C2–C3	1.410	C1–C2–C3	121.3
C1–C7	1.505	C2–C1–C6	117.5
C1–Mn	2.176	Mn–C1–C2	69.7
C2–Mn	2.145	Mn–C2–C3	70.8
C3–Mn	2.145	C1–Mn–C2	38.2
		C2–Mn–C3	38.4

Table 2b
Bond lengths and angles for bis(p-xylene) manganese (I) in the D_{2h} configuration

Bond length (Å)		Angle (°)	
C1–C2	1.410	C7–C1–C2	121.1
C2–C3	1.414	C1–C2–C3	121.1
C1–C7	1.504	C2–C1–C6	117.7
C1–Mn	2.189	Mn–C1–C2	69.4
C2–Mn	2.148	Mn–C2–C3	70.8
C3–Mn	2.148	C1–Mn–C2	38.1
		C2–Mn–C3	38.3

is an electronic delocalization. For bis([2,2]-p-cyclophane) manganese (I), the optimized geometry of the molecule belongs to the D_2 point group Tables 2a,b and 3a–c, with the cyclophanes making a dihedral angle of

Table 3a
Bond lengths and angles for bis([2,2]-p-cyclophane) manganese (I) in the minimum energy configuration [a]

Bond length (Å)		Angle (°)	
C1–C2	1.400	C1–C2–C3	120.6
C2–C3	1.393	C2–C1–C6	117.0
C1–C6	1.400	C1–C6–C5	120.7
C1–C7	1.515	C2–C1–C7	120.9
C7–C8	1.615	C1–C7–C8	113.5
C8–C11	1.508	C7–C8–C11	110.7
C11–C12	1.412	C8–C11–C12	121.3
C12–C13	1.417	C11–C12–C13	120.4
C11–C16	1.408	C12–C11–C16	116.9
C11–Mn	2.287	C11–C16–C15	120.4
C12–Mn	2.120	Mn–C11–C12	65.0
C16–Mn	2.131	Mn–C12–C13	71.0
C1–C11	2.754	Mn–C16–C15	70.1
C2–C12	3.107	C11–Mn–C12	37.1
C6–C16	3.094	C12–Mn–C13	38.9
		C11–Mn–C16	37.0

[a] This is a reduce set, other distances and angles are obtained by symmetry.

Table 3b
Bond lengths and angles for bis([2,2]-p-cyclophane) manganese (I) in the D_{2d} configuration

Bond length (Å)		Angle (°)	
C1–C2	1.400	C1–C2–C3	120.7
C2–C3	1.393	C2–C1–C6	116.9
C1–C7	1.516	C2–C1–C7	121.0
C7–C8	1.615	C1–C7–C8	113.7
C8–C11	1.508	C7–C8–C11	110.8
C11–C12	1.412	C8–C11–C12	121.0
C12–C13	1.409	C11–C12–C13	120.6
C11–Mn	2.277	C12–C11–C16	117.2
C12–Mn	2.137	Mn–C11–C12	66.0
C1–C11	2.762	Mn–C12–C13	70.7
C2–C12	3.084	C11–Mn–C12	37.1
		C12–Mn–C13	38.5

Table 3c
Bond lengths and angles for bis([2,2]-p-cyclophane) manganese (I) in the D_{2h} configuration

Bond length (Å)		Angle (°)	
C1–C2	1.400	C1–C2–C3	120.7
C2–C3	1.393	C2–C1–C6	116.9
C1–C7	1.516	C2–C1–C7	121.0
C7–C8	1.616	C1–C7–C8	113.8
C8–C11	1.508	C7–C8–C11	110.8
C11–C12	1.412	C8–C11–C12	120.9
C12–C13	1.409	C11–C12–C13	120.5
C11–Mn	2.274	C12–C11–C16	117.4
C12–Mn	2.137	Mn–C11–C12	66.1
C1–C11	2.762	Mn–C12–C13	70.8
C2–C12	3.083	C11–Mn–C12	37.2
		C12–Mn–C13	38.5

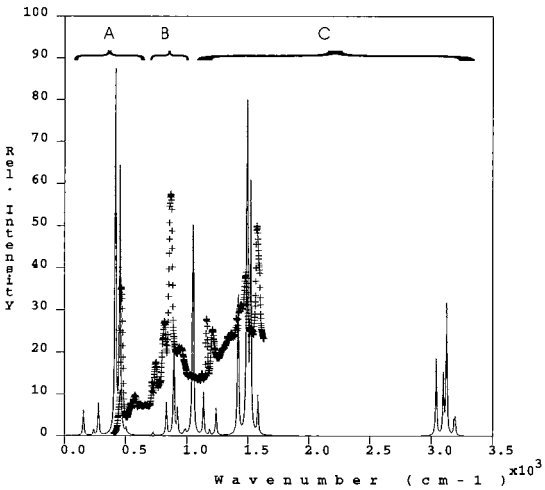


Fig. 2. Experimental infrared spectrum of Mn–poly-*p*-xylylene and theoretical infrared spectrum of bis(*p*-xylene) manganese (I).

50.5°. The inner and outer rings are not flat, and the torsion angles are 16.5 and −14.7°, respectively. Nevertheless, the bond lengths in the rings are very regular with a maximum angle distortion of 3.1°, this again indicates an electronic delocalization in the rings. For the inner rings there are four carbons at about the same distance to the metal (2.120 and 2.131 Å) and two more slightly farther away at 2.287 Å. The theoretical infrared spectrum of bis(*p*-xylene) manganese (I) is compared with the experimental spectrum [44] of Mn–poly-*p*-xylylene in Fig. 2. The theoretical results show that the region A (low frequencies) corresponds to vibrations of the Mn and the carbons in the rings. The middle region to vibrations of the hydrogen atoms in the rings and the region C (high frequencies) to the methyl groups (C–H vibrations are at high frequencies). It is to be expected that the difference between the solid phase (experimental) and the gas phase (theory) should be in the interchain interactions and, thus, that the methyl vibrational frequencies would be modified. As can be seen, there is a good agreement between both spectra in regions A and B, the main differences are in region C where the interchain interactions are expected to be important.

For both compounds, the energy difference between D_2, D_{2d} and D_{2h} structures is small. The changes in bond lengths and angles when going from one configuration to another are very small. With this results, it is not possible to assure that one structure is more stable than the other. The behavior of both structures is quite similar and for this reason, further discussion of the results will be made using the D_{2d} structures.

The Mülliken charge analysis is given in Table 1. For bis(*p*-xylene) manganese (I) the manganese is positively charged (0.86), while the six-member rings are negatively charged (−0.31, including the hydrogen atoms). Fig. 3 shows the charge density contours in three different orientations for this compound, the bonds in the ring presents a typical overlap structure, while the bonds between the Mn and the rings does not show a high electron concentration. Another notable feature, is the negative charge on the carbon atom of the methyl group. This suggests that the ring has some quinoid character as was suggested earlier [47]. The same behavior is observed in the D_{2h} structure, see Table 1.

Additionally, in Table 1, the Mülliken charge analysis for bis([2,2]-*p*-cyclophane) manganese (I) is given. The Mn has a positive charge (0.921) and the inner rings are negatively charged (−0.332). The outer rings are almost neutral and the carbon atoms of the ethylene bridges have a negative charge (−0.172, −0.153). As can be seen in the same Table 1, the behavior for the D_{2h} structure is quite similar.

Fig. 4 shows the charge density contours for bis([2,2]-*p*-cyclophane) manganese (I) in two different orientations. In this case, the bonding within the cyclophanes is the typical covalent bond, and the bond between the cyclophane and the Mn is a π bond. The shape of the charge clouds has the same form as the electronic flow path, from the outer ring to the central metal atom. This is further evidence of the transanular electronic interaction between both rings, and this compels the

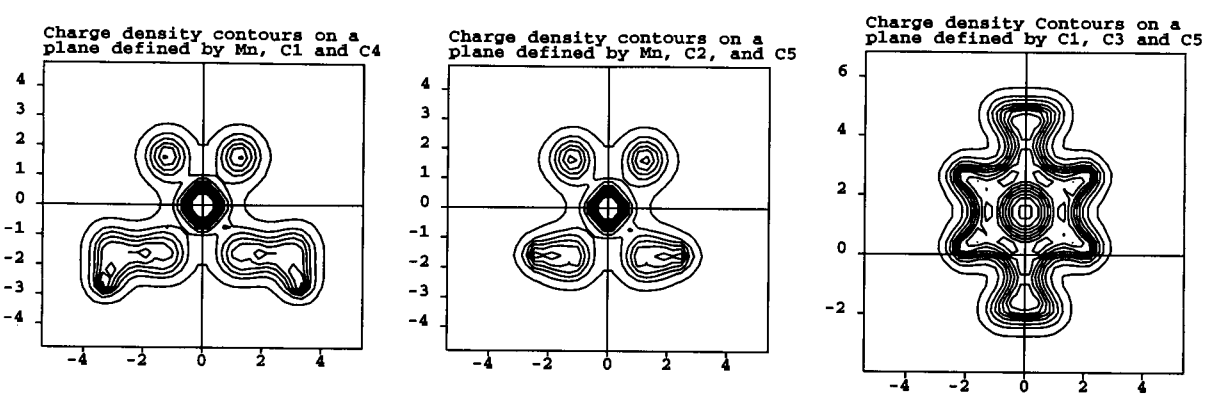


Fig. 3. Charge density contours for three different orientations for bis(*p*-xylene) manganese (I).

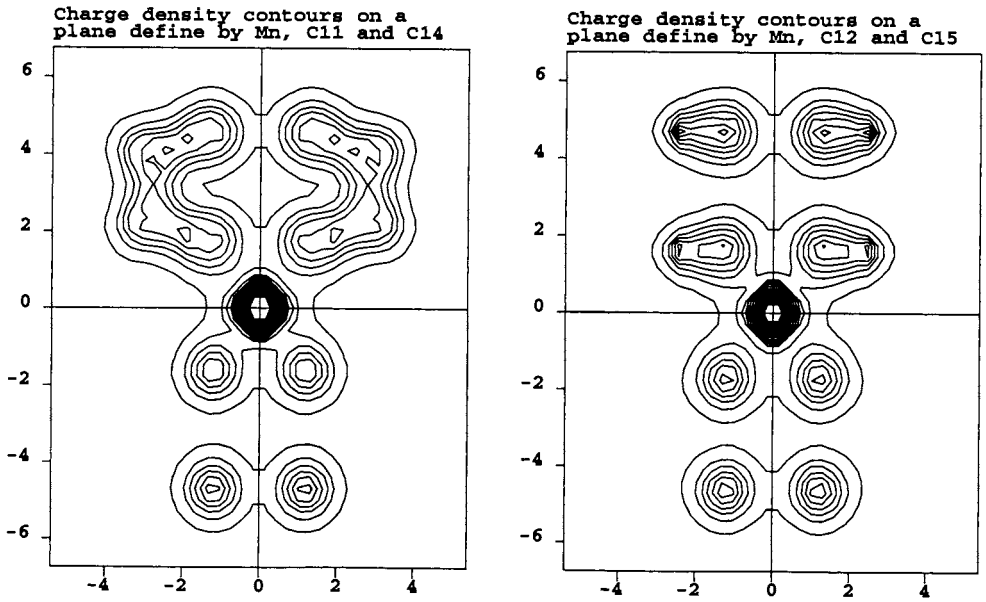


Fig. 4. Charge density contours for two different orientations for bis([2,2]-*p*-cyclophane) manganese (I).

electrons to go toward the metal atom due to the big positive charge in this region.

Fig. 5 shows the variation of the total energy as a function of the dihedral angle between the methyl substituents for bis(*p*-xylene) manganese (I) and between the cyclophanes for bis([2,2]-*p*-cyclophane) manganese (I).

For bis(*p*-xylene) manganese (I) there is no pseudorotational barrier. The energy difference between the D_{2d} (0° dihedral angle) and the D_{2h} (90° dihedral angle) configurations is only 0.85 kcal mol^{-1}. This is due to the delocalized charge and an interchange of form between the quinoid and aromatic types of the rings. The quinoid form has a high negative charge density on the methyl groups, and this generates repulsion between the pairs of this groups localized face to face on both rings, and it is this effect that causes the rotation. Moreover, this means that the bonding between the metal and the rings is delocalized. The energetic barrier for bis([2,2]-*p*-cyclophane) manganese (I) is 2.04 kcal mol^{-1}, which can be considered a low value, and that the process of interconversion may be possible. The important point is that this can not be considered as a rotational barrier, but a kind of fluxional isomerism (a real rotational barrier is considered when the size is greater than 5 kcal mol^{-1}).

Fluxional isomerism is a phenomenon not commonly found in 6-organometallic compounds. For bis([2,2]-*p*-cyclophane) manganese (I) the effect arises for different reasons. Due to the transannularity effect (this will be explained later in more detail) we have extra charge on the inner rings that bonds to the metal atom, these same charges are also on the six member ring but the ring is slightly distorted (boat shape). Furthermore there are two sets of carbon atoms, the first one, is made up of the four central carbon atoms that generate a plane and the second group, by the two atoms that are slightly shifted (the carbon metal bond length is 2.12 Å for the first set and 2.287 Å for the second set). The charge is about the same for the six atoms −0.13. Based on this, it is possible that the ring is bonded to the metal in an η^4 fashion (the first set) but the atoms in the second set would like to partcipate in the bonding, giving up some charge, and breaking the η^4 bond to form an η^6, and this implies a brief rupture that allows the rearrangement.

In order to understand the transannular effect and the fluxional isomerism present in compound **2** we have carried out a molecular orbital analysis. In Fig. 6 the molecular orbital picture of bis(*p*-xylene) manganese (I)

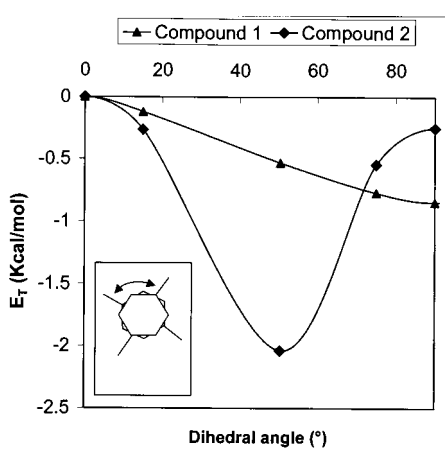


Fig. 5. Pseudorotational barrier of bis(*p*-xylene) manganese (I) (Compound **1**) and bis([2,2]-*p*-cyclophane) manganese (I) (Compound **2**). The total energy is shown as a function of dihedral angle.

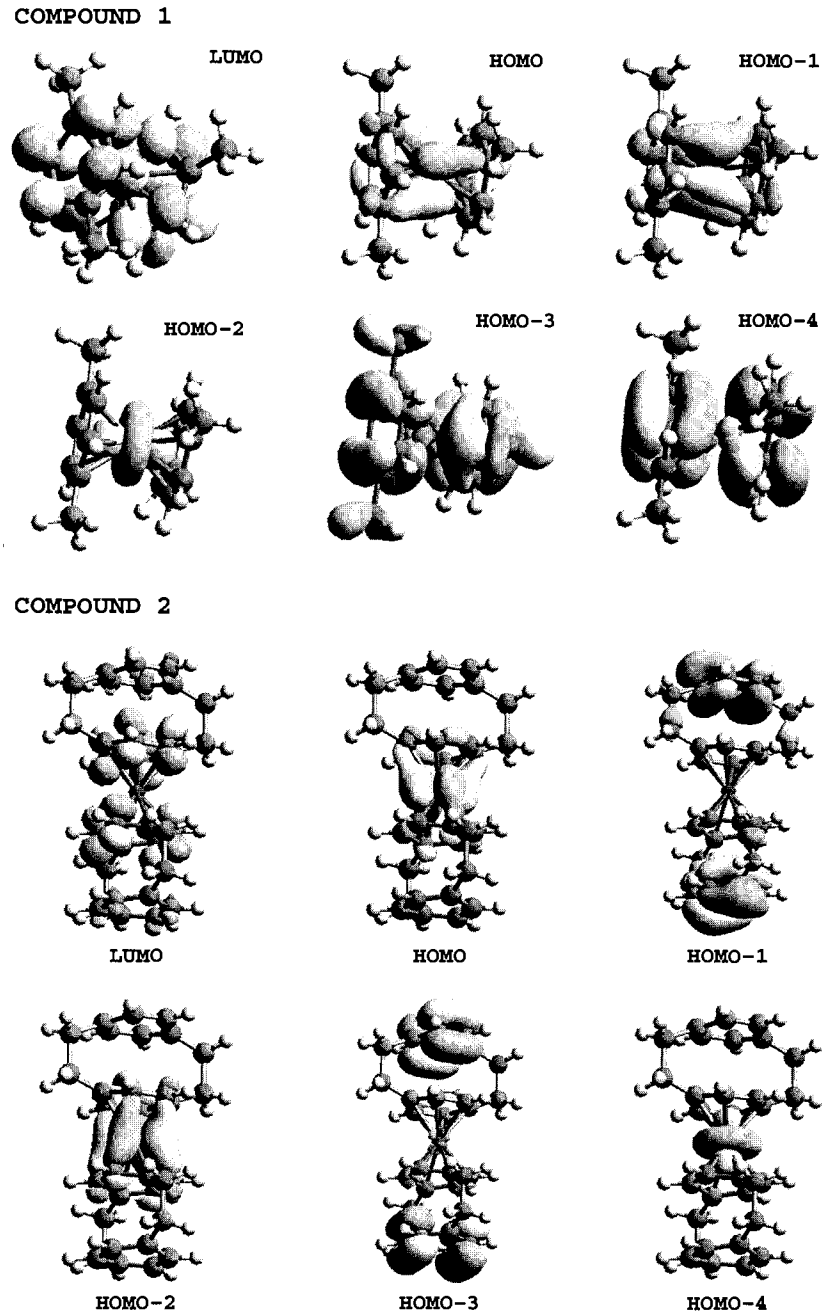


Fig. 6. Molecular orbital picture for bis(*p*-xylene) manganese (I) (Compound **1**) and bis([2,2]-*p*-cyclophane) manganese (I) (Compound **2**). The degenerate orbitals with an e irreducible representation are drawn together.

and bis([2,2]-*p*-cyclophane) manganese (I), is shown and Fig. 7 shows the corresponding molecular orbital eigenvalues diagram. For both compounds, the highest occupied molecular orbital (HOMO) is located mainly on the Mn atom and it forms a bridge between the two rings. The HOMO belongs to the b_2 irreducible representation, and it has a big contribution from the d_{xy} orbital of the metal. The bond between metal and ligands is located in these orbitals. Both orbitals present the same bonding situation and symmetry.

The lowest unoccupied molecular orbital (LUMO) of bis(*p*-xylene) manganese (I) is mainly localized at the ring and belongs to the a_2 irreducible representation. It is an antibonding π^* orbital. For bis([2,2]-*p*-cyclophane) manganese (I) the LUMO is similar.

The HOMO-1 of bis([2,2]-*p*-cyclophane) manganese (I) is mainly localized at the outer rings. This orbital belongs to the e irreducible representation, indicating that they are two-fold degenerated sets of orbitals. The HOMO-2 orbital of this compound is a b_1 orbital and is localized mainly at the $d_{x^2-y^2}$ of the metallic atom

and on the inner rings. This orbital is similar to the HOMO-1 of bis(*p*-xylene) manganese (I).

The molecular orbital picture indicate that the HOMO-2 orbital of bis(*p*-xylene) manganese (I) is similar to the HOMO-4 orbital of bis([2,2]-*p*-cyclophane) manganese (I), and they are the d_{z^2} of the Mn.

To understand the transannular effect we have to analyze the LUMO, HOMO and nearby orbitals of the three configurations. Fig. 8 shows the MO spliting of the three conformations. For the D_2 conformation the

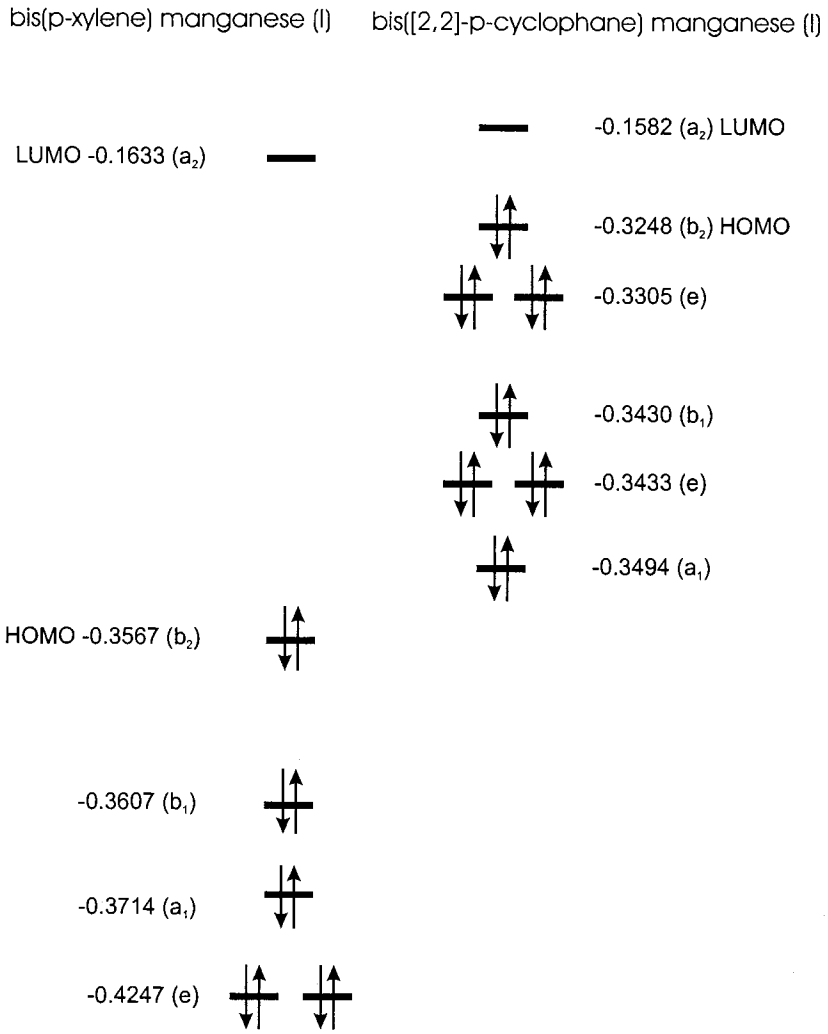


Fig. 7. Molecular orbital eigenvalue diagrams for bis(*p*-xylene) manganese (I) and bis([2,2]-*p*-cyclophane) manganese (I) in the D_{2h} configuration. The units are in hartree.

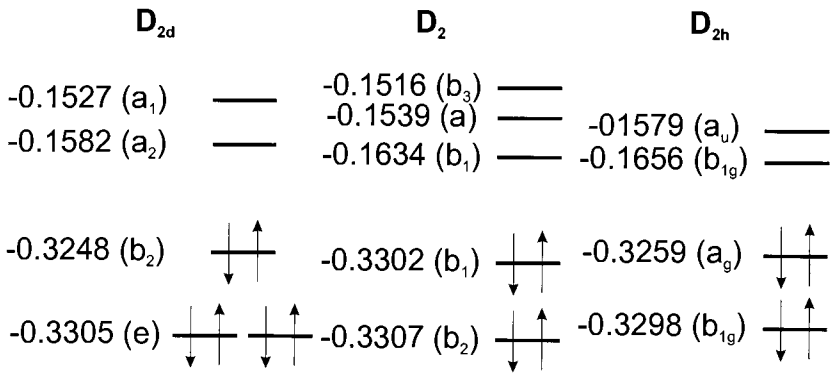


Fig. 8. Molecular orbital eigenvalue diagram for the three configurations of bis([2,2]-*p*-cyclophane) manganese (I). The units are in hartree.

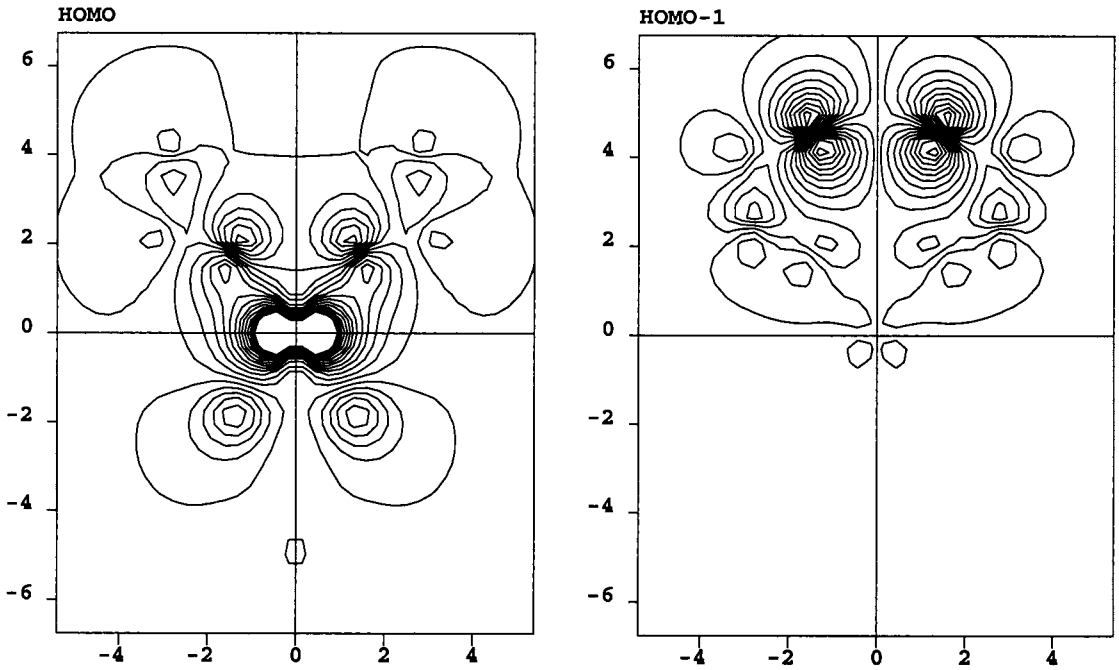


Fig. 9. Contour plots of the HOMO and HOMO-1 of bis([2,2]-*p*-cyclophane) manganese (I).

LUMO + 1 and LUMO + 2 (0.26 and 0.33 eV. over the LUMO and belonging to a and b_3 representation, respectively) arise from contributions of the carbons in the inner and outer rings, the LUMO (belonging to b_1) arise from the metal d_{xy} atomic function and the carbons of the inner rings and the HOMO (b_1 representation) from the carbons on the outer rings. The LUMO + 1 (0.21eV. over the LUMO and a_u representation) arises from contributions of the carbons in the inner and outer rings, the LUMO (belonging to b_{1g}) arises from the metal d_{xy} atomic function and the carbons of the inner rings, and the HOMO (a_g representation) from the metal and carbons on the inner ring. The D_{2d} LUMO (a_2 representation) main contributions, are from the carbons on the inner and outer rings and the HOMO (b_2 representation) from the metal and carbons on the inner ring. For all three configurations the HOMO-1 (belonging to b_2, b_{1g} and e representations for the D_2, D_{2h} and D_{2d} configurations respectively) is mainly located on the carbons on the outer rings. The HOMO and HOMO-1 orbitals are separated by 0.0016 hartree (0.0435 eV.) in the D_{2d} and 0.00391 hartree (0.106 eV.) in the D_{2h}. In Fig. 9, we show the contour plot of both orbitals for the D_{2d} configuration, an overlap between them can be seen. This means that in the three configurations there is a channel through which electrons can be transferred from one side of the molecule to the other and thus the transannular effect is present. This situation arises because the manganese ion has the behavior of an electronic release center that compels the electron motion from the outer ring to the center of the molecule and to the inner ring which is bonded to the metal. In other words, there is a delocalization of the electrons at a molecular level. This is similar to that shown by Dyson et al. [48] for free [2,2]*para*-cyclophane, who showed from a theoretical point of view, that the transannular effect is mainly a consequence of the electronic π–π repulsion between both decks with very little participation of electronic flow through bonds (via the bridges).

4. Conclusions

In this paper, we presented the optimized geometries of bis(*p*-xylene) and bis([2,2]-*p*-cyclophane) manganese (I). Both molecules are cations with a positive (+1) charge and follow the 18 electron rule. The optimized geometries show that bis(*p*-xylene) manganese (I) belong to the D_{2d} point group while bis([2,2]-*p*-cyclophane) manganese (I) to the D_2 with a dihedral angle between the cyclophanes of 50.5°. For both compounds, the energy difference between D_{2d} and D_{2h} is

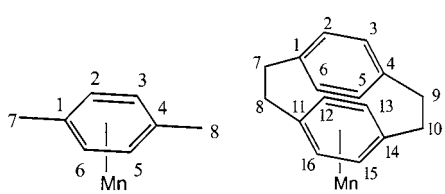


Fig. 10. Notation used in Tables 2a, 2b, 3a, 3b and 3c for both compounds

small. From these results it is not possible to assure that one structure is more stable than the other. However, the behavior of both compounds is similar.

For bis(*p*-xylene) manganese (I), there is no pseudorotational barrier, and the rings in this compound have a delocalized charge and an aromatic behavior. This means that the bonding between the metal and the rings is delocalized.

The energetic barrier for bis([2,2]-*p*-cyclophane) manganese (I) is 2.04 kcal mol^{-1}. This can be considered as a kind of fluxional isomerism. In bis([2,2]-*p*-cyclophane) manganese (I), due to the transannularity effect, we have extra charge on the inner rings that allows electronic motion and thus the rotation of the bonds between these rings and the metal.

There is good agreement between the theoretical infrared spectrum of bis(*p*-xylene) manganese (I) and the experimental spectrum of Mn–poly-*p*-xylylene.

Analyzing the molecular orbital pictures, we can see that for bis(*p*-xylene) manganese (I), the HOMO has a large contribution from the metal atomic orbitals, with the same being true for the bis([2,2]-*p*-cyclophane) manganese (I). In bis([2,2]-*p*-cyclophane) manganese (I) a bridge between the rings is formed and this explains the electric flow.

Much of the evidence indicates that the transannular electronic interaction for bis([2,2]-*p*-cyclophane) manganese (I) is possible. There is a strong electronic charge accumulation on the inner ring. The manganese ion has the behavior of an electronic release center that compels electronic motion from the outer ring to the center of the molecule. For all three configurations there is a bridge between the rings, in such a way, that the electronic density can flow from one side of the molecule to the other.

The electronic density map of bis([2,2]-*p*-cyclophane) manganese (I) shows that the biggest electronic contribution is located at the center of the molecule, i.e. within the environment of the metal, and there is a continuos flow of density from the outer ring towards this center.

Acknowledgements

We thank Conacyt (grant 3157PA) and Dirección General de Asuntos del Personal Académico, UNAM (grant IN101597) for financial support. We would like to acknowledge the Dirección General de Computo Académico at UNAM for providing computer time.

References

[1] E. Heilbronner, Z. Yang, Top. Curr. Chem. (1984) 115.
[2] F. Gerson, Top. Curr. Chem. (1984) 115.
[3] M. Rosenblum, H.M. Nugent, K.S. Jang, M.M. Labes, W. Cahalane, P. Klemarczyk, W.M. Reiff, Macromolecules 28 (1995) 6330.
[4] L.N. Alexandrova, V.A. Sochilin, G.N. Gerasimov, I.E. Kardash, Polymer 38 (1997) 721.
[5] R.T. Swann, V. Boekelheide, Tetrahedron Lett. 25 (1984) 899.
[6] R.T. Swann, A.W. Hanson, V. Boekelheide, J. Am. Chem. Soc. 106 (1984) 818.
[7] E.D. Laganis, R.G. Finke, V. Boekelheide, Tetrahedron Lett. 21 (1980) 4405.
[8] R.T. Swann, A.W. Hanson, V. Boekelheide, J. Am. Chem. Soc. 108 (1986) 3324.
[9] E.D. Laganis, R.H. Voegeli, R.T. Swann, R.G. Finke, H. Hopf, V. Boekelheide, Organometallics 1 (1982) 1415.
[10] W.M. Lamanna, J. Am. Chem. Soc. 108 (1986) 2096.
[11] C. Elschenbroich, R. Möckel, U. Zenneck, Angew. Chem. Int. Ed. Engl. 17 (1978) 531.
[12] R. Gleiter, D. Kratz, Acc. Chem. Res. 26 (1993) 311.
[13] J.E. Garbe, V. Boekelheide, J. Am. Chem. Soc. 105 (1983) 7384.
[14] W.D. Rohrbach, V. Boekelheide, J. Org. Chem. 48 (1983) 3673.
[15] V. Boekelheide, Pure Appl. Chem. 58 (1986) 1.
[16] M.R.J. Elsegood, D.A. Tocher, Inorg. Chim. Acta 161 (1989) 147.
[17] K.D. Plitzko, B. Rapko, B. Gollas, G. Wehrle, T. Weakley, D.T. Pierce, W.E. Geiger Jr., R.C. Haddon, V. Boekelheide, J. Am. Chem. Soc. 112 (1990) 6545.
[18] K.D. Plitzko, G. Wehrle, B. Gollas, B. Rapko, J. Damheim, V. Boekelheide, J. Am. Chem. Soc. 112 (1990) 6556.
[19] J.W. Steed, D.A. Tocher, J. Chem. Soc. Dalton Trans. (1993) 3187.
[20] J.W. Steed, D.A. Tocher, Proc. Indian Acad. Sci. (Chem. Sci.) 106 (1994) 691.
[21] A.J. Blake, P.J. Dyson, S.L. Ingham, B.F.G. Johnson, C.M. Martin, Organometallics 14 (1995) 862.
[22] D.J. Cram, D.I. Wilkinson, J. Am. Chem. Soc. 82 (1960) 5721.
[23] H. Ohno, H. Horita, T. Otsubo, Y. Sakata, S. Misumi, Tetrahedron Lett. (1977) 265.
[24] M. Hisatome, O. Tachikawa, M. Sasho, K. Yamakawa, J. Organomet. Chem. 217 (1981) C17.
[25] A. Kasahara, T. Izzumi, Y. Yoshida, Y. Shimizu, Bull. Chem. Soc. Jpn. 55 (1982) 1901.
[26] H. Hopf, J. Damheim, Angew. Chem. Int. Ed. Engl. 27 (1988) 701.
[27] M. Hisatome, M. Yoshihashi, K. Yamakawa, Y. Ittaka, Bull. Chem. Soc. Jpn. 60 (1987) 2953.
[28] P. Jutzi, U. Siemeling, A. Müller, H. Bögge, Organometallics 8 (1989) 1744.
[29] C.M. Adams, E. Holt, Organometallics 9 (1990) 980.
[30] D.J. Cram, J.M. Cram, Acc. Chem. Res. 4 (1971) 204.
[31] D.J. Cram, N.L. Allinger, H.J. Steinberg, J. Am. Chem. Soc. 76 (1954) 6132.
[32] D.J. Cram, M.J. Sheehan, J. Am. Chem. Soc. 91 (1969) 3553.
[33] R. Gleiter, M. Karcher, M.L. Ziegler, B. Nuber, Tetrahedron Lett. 28 (1987) 195.
[34] K.D. Plitzko, V. Boekelheide, Organometallics 7 (1988) 1573.
[35] Y. Sekine, V. Boekelheide, J. Am. Chem. Soc. 101 (1979) 3126.
[36] R. Gleiter, H. Langer, V. Schehlmann, B. Nuber, Organometallics 14 (1995) 975.
[37] R. Gleiter, V. Schehlmann, Angew Chem. Int. Ed. Engl. 29 (1990) 1426.
[38] R. Gleiter, D. Kratz, Tetrahedron Lett. 31 (1990) 5893.
[39] J.S. Thayer, Adv. Organometal. Chem. 13 (1975) 1.
[40] V. Boekelheide, Acc. Chem. Res. 13 (1980) 65.
[41] K.J. Klabunde, Chemistry of Free Atoms and Particles, Academic, New York, 1980, pp. 60–65.
[42] J.R. Blackborrow, D. Young, Metal Vapour Synthesis in Organometalic Chemistry, Springer-Verlag, New York, 1979, pp. 119–136.

[43] W.E. Billups, A.W. Moorehead, P.J. Ko, J.L. Margrave, J.P. Bell, F.B. McComrmick, Organometallics 7 (1988) 2230.
[44] L. Alexandrova, D. Likhatchev, S. Muhl, R. Salcedo, G. Gerasimov, I. Kardash, J. Inorg. Organomet. Pol. 8 (1998) 157.
[45] E.O. Fischer, S. Breitschaft, Chem. Ber. 99 (1966) 2213.
[46] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker and J.P. Pople, Gaussian Inc., Pittsburg, P.A. 1995.
[47] L. Alexandrova, R. Salcedo, Polymer 35 (1994) 4656.
[48] P.J. Dyson, D.G. Humprey, J.E. McGrady, M.P. Mingos, J. Wilson, J. Chem. Soc. Dalton Trans. (1995) 4039.