PHYSICAL REVIEW A **83**, 022507 (2011)

Multilayer cyclic C_6 structures intercalated with metal atoms

Stanislav Kuzmin[*] and Walter W. Duley

Department of Physics and Astronomy, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, N2L 3G1 Canada

(Received 18 August 2010; published 24 February 2011)

A new type of tubular inorganic metal-carbon sandwich molecule based on cyclic C_6 is proposed. These consist of multiple layers of cyclic C_6 with intercalated metal atoms. Structures and electronic properties of these molecules have been calculated using first-principles density functional techniques. We have evaluated all metals in the first six periods of the periodic table, except for the lanthanides, as possible components of such molecules. Our calculations show high bond energy and small energy gaps in many of these structures. We suggest that the high structural stability and high conductivity in these sandwich compounds make them very promising for use in nanoelectronic applications.

DOI: 10.1103/PhysRevA.83.022507 PACS number(s): 31.15.A−, 33.15.Fm, 81.05.U−

I. INTRODUCTION

First-principles calculations of the geometry and properties of cyclic C_6 have been reported in many papers [1–10,15–17] over the past 20 years. There have also been a number of experimental studies of the spectra of C_6 molecules in matrices [11–14]. These show that there are two isomers of cyclic C_6, one in which the ground state has D_{3h} symmetry and another at slightly higher energy with D_{6h} symmetry. This is confirmed by additional calculations based on the Becke three-parameter Lee-Yang-Parr hybrid functional (B3LYP) 6-311G method that show that the energy difference between these two configurations is ≈0.41 eV [15]. Although the geometry of cyclic C_6 is similar to that of the benzene molecule, the orbital structure differs substantially between the two molecules [15]. In benzene, delocalized electrons are located in aromatic rings on each side of the molecular plane, whereas in cyclic C_6 the highest occupied molecular orbital (HOMO) is localized to the plane of the molecule The differences between orbital distributions in benzene and in cyclic C_6 makes it possible for cyclic C_6 to form metal-sandwich compounds that would be unstable in systems based on benzene [17].

Metal-benzene compounds have been the subject of much interest since the discovery of V-benzene polymers [18] and many theoretical [19–24,28,32–35] and experimental [25–27,31] studies of the properties of these molecules have been reported. These molecules are of special interest because of their unique electronic and magnetic properties [19–21,23,28,29,33,35]. For example, metal-benzene polymers are expected to be good conductors for spin transport [20,28,29] and as components in novel nanoscale devices. It has been suggested that multilayered sandwich molecules based on benzene combined with Ti, Cr, Sc, Fe, Ni, Nb, Ta, and Mn are possible [19,23,24,29,31–33] but, to date, such structures have been found only in V-benzene systems. A number of interesting electronic and magnetic properties of the multilayered sandwich V-benzene molecules have been identified [20,21,23,29]. All these types of molecule studied so far have been insulators with energy gaps exceeding 3 eV.

In this article we propose a new structure based on layers of cyclic C_6 intercalated with metal atoms. *Ab initio* calculations show the possibility for the existence of a variety of polymeric inorganic metal-carbon molecules in which C_6 is combined with different metals. We find that the most promising structures involve C_6 in combination with group VIII transition metals, specifically Fe, Ru, and Os, and some adjacent elements, including V, Mn, Tc, Re, and Ir, in the periodic table. Other partners include the alkali metals (Li, Na, K, Rb) as well as some alkaline earth metals (Mg, Ca, Ba). Be and Hg can also form similar molecules with help of van der Waals forces. The most energetically stable molecules are those involving Fe and Ru. In general, we find that there is a correlation between increasing stability in MC_6 molecules, where M denotes metal, and the atomic weight of the metal. Stability also increases with the overall length of the molecule.

All calculations of the geometry, electronic properties and vibrational properties of these compounds were carried out with GAUSSIAN-03/09 [30] using the most precise DFT methods consistent with computational efficiency. For molecules incorporating Li, K, Ca, Fe, Mn, and V calculations were carried out on a B3LYP/6-311G∗ and B3LYP/6-31G∗ basis. For molecules incorporating heavier metals a Becke three-parameter Perdew-Wang 1971 functional/Los Alamos National Laboratory 2-double-zeta (density functional theory) (B3PW91/LANL2DZ) basis was used.

II. GEOMETRY AND STABILITY OF THE CHEMICAL BONDS

According to recent reports [25–27,31], of all the elements in the first four periods of the periodic table, only V can form long stable sandwich molecules with benzene. On the basis of the present study, we find that many more atoms can form sandwich molecules based on cyclic C_6. In particular, Li, K, Ca, Na, Fe, V, Mg, and Mn all combine in this way with cyclic C_6. The highest-stability compounds are those incorporating Fe in a $(C_6)_nFe_{n-1}$ structure, whereas $(C_6)_nMn_{n-1}$ sandwich molecules appear to be less stable because the cyclic C_6 rings are distorted in these compounds. $(C_6)_nV_{n-1}$ molecules are found to be stable only when $n \geqslant 4$ and $(C_6)_nMg_{n-1}$ is stable only with $n = 3$ as $(C_6)_5Mg_4$ and $(C_6)_3Mg_2$ are both unstable. For groups 1 and 2 atoms, Table I shows that the $Li(C_6)$ bond energy is much smaller than the $Me(C_6)$ bond energy in other molecules, so these molecules have marginal stability. In addition, we find that molecules incorporating Ca,

---

[*] stan@kuzmin.ca

K, and Na are asymmetric, indicating that they may tend to be unstable. Among elements in the fifth and sixth periods, only Rb, Ba, Tc, and Ru compounds are found to form stable molecules $(C_6)_n M_{n-1}$. Some other elements, notably Cs, Re, Os, and Ir, form stable molecules, but often their structures are distorted or the order of symmetry is lowered. Absence of the stable metalorganic polymer molecules with two, three, or four C_6 layers or low symmetry in these molecules shows the unsaturated character of the metal-C_6 bonds that indicates hyper chemical activity of polymer molecules with such metal atoms. Hence, for metalorganic molecules with such metals the structural instability caused by chemical hyper activity could occur.

We find that the symmetry of individual cyclic C_6 rings in these molecules is either C_6 or C_3. While one expects rings with C_3 symmetry to be more stable, our calculations indicate that the most stable overall structures involve cyclic C_6 rings in which the symmetry is C_6. This occurs because of strong aromatic bonding within the ring. The overall symmetry of $(C_6)_n M_{n-1}$ molecules is related to the symmetry of individual cyclic C_6 rings and their relative orientation (Fig. 1). In the most symmetric molecules, where the overall symmetry is D_{6h}, the intrinsic symmetry of cyclic C_6 is C_6 and all rings have the same orientation relative to the axis of the molecule. All long molecules incorporating Fe and Ru are examples of this type. If the orientation of cyclic C_6 with symmetry C_6 is not regular, for example, as in $(C_6)_3Li_2$, then we find that the overall symmetry becomes C_3. Another configuration occurs when two or more cyclic C_6 have C_3 symmetry and all the cyclic rings are oriented in the same way, then the molecule has D_{3h} symmetry. This structure occurs in $(C_6)_3Fe_2$. This reduces to C_3 symmetry when all the cyclic rings have different orientations. Some examples of structures that are subject to different distortions induced by constraints on bonding are shown in Fig. 2.

Tables I and II summarize the symmetries and bond energies for different MC_6 sandwich molecules. We can see that molecules incorporating alkali metals are less strongly bonded than those involving transition metals. The average Mulliken charge on the metal atom in this case, with the exception of Li, is ≈0.8–0.9 of an electron. As the rings in these molecules have C_3 symmetry, it is apparent that aromatic bonding is less important in these molecules and that the MC_6 bond is primarily ionic. A summary of MC_6 bond energies in $(C_6)_3 M_2$ is shown in Fig. 3. It should be noted that the alkaline-earth metals form strong bonds but show some structural instability. This can be attributed to the tendency for a strong interaction to develop between the metal atom and a single carbon atom in the ring which causes a direct bond to form between them. In general, we find that average bond energy is well correlated

TABLE I. Geometry and bond parameters in metal-organic molecules $(C_6)_n Me_{n-1}$ with $n = 3,4$

Structure	Calculation method	Molecular symmetry	Average bond length between two cyclic C_6 (Å)	Average length of the bond in cyclic C_6 in the central ring (Å)	Average metal-C_6 bond energy (eV)	Average Mulliken charge on metal atom	Presence of structural distortion
$(C_6)_3Fe_2$	B3LYP/6-311G∗	D_{3h}	3.15	1.4	10.29	0.833	
$(C_6)_3K_2$	B3LYP/6-311G∗	C_3	5.783	1.36	3.73	0.801	
$(C_6)_3Li_2$	B3LYP/6-311G∗	C_6	4.034	1.371	0.22	0.196	
$(C_6)_3Ca_2$	B3LYP/6-311G∗	C_3	4.834	1.402	12.048	1.274	
$(C_6)_3Na_2$	B3LYP/6-311G∗	D_{3h}	4.96	1.36	2.97	0.662	
$(C_6)_3Ba_2$	B3PW91/LANL2DZ	C_3	5.77	1.408	9.897	1.807	
$(C_6)_3Cs_2$	B3PW91/LANL2DZ	C_3	6.92	1.37	3.58	0.924	
$(C_6)_3Ir_2$	B3PW91/LANL2DZ	D_{6h}	3.56	1.47	8.69	1.148	
$(C_6)_3Mn_2$	B3LYP/6-311G∗	C_{2h}	3.32	1.396	8.66	0.869	∗
$(C_6)_3Os_2$	B3PW91/LANL2DZ	D_{6h}	3.57	1.466	4.468	0.939	
$(C_6)_3Rb_2$	B3PW91/LANL2DZ	D_{3h}	6.53	1.37	3.68	0.911	
$(C_6)_3Re_2$	B3PW91/LANL2DZ	Near D_2	3.6	1.46	10.84	0.523	∗
$(C_6)_3Ru_2$	B3PW91/LANL2DZ	D_{6h}	3.59	1.45	17.93	0.615	
$(C_6)_3Tc_2$	B3PW91/LANL2DZ	Near D_{6h}	3.6	1.46	5.571	0.625	∗
$(C_6)_4Fe_3$	B3LYP/6-311G∗	D_{3h}	3.19	1.41	11.63	0.836	
$(C_6)_4K_3$	B3LYP/6-311G∗	C_3	5.76	1.36	2.33	0.644	∗
$(C_6)_4Li_3$	B3LYP/6-311G∗	D_{3h}	4.12	1.36	2.94	0.229	∗
$(C_6)_4Ba_3$	B3PW91/LANL2DZ	C_3	5.92	1.41	9.73	1.898	
$(C_6)_4Cs_3$	B3PW91/LANL2DZ	C_3	6.92	1.37	1.94	0.933	
$(C_6)_4Ir_3$	B3PW91/LANL2DZ	Near D_{6h}	3.77	1.41	2.96	1.132	∗
$(C_6)_4V_3$	B3LYP/6-311G∗	Near D_{3d}	3.67	1.4	5.39	0.976	
$(C_6)_4Mn_3$	B3LYP/6-311G∗	C_2v	3.09	1.39	2.38	0.872	∗
$(C_6)_4Mg_3$	B3LYP/6-31G∗	$\approx D_{3d}$	3.97	1.4	1.8	0.104	
$(C_6)_4Rb_3$	B3PW91/LANL2DZ	Near D_{3h}	6.46	1.37	2.19	0.927	
$(C_6)_4Ru_3$	B3PW91/LANL2DZ	D_{6h}	3.57	1.46	3.78	0.892	
$(C_6)_4Tc_3$	B3PW91/LANL2DZ	D_{6h}	3.54	1.46	5.45	0.916	
$(C_6)_3Fe_2$	B3LYP/6-311G∗	D_{3h}	3.15	1.4	10.29	0.833	

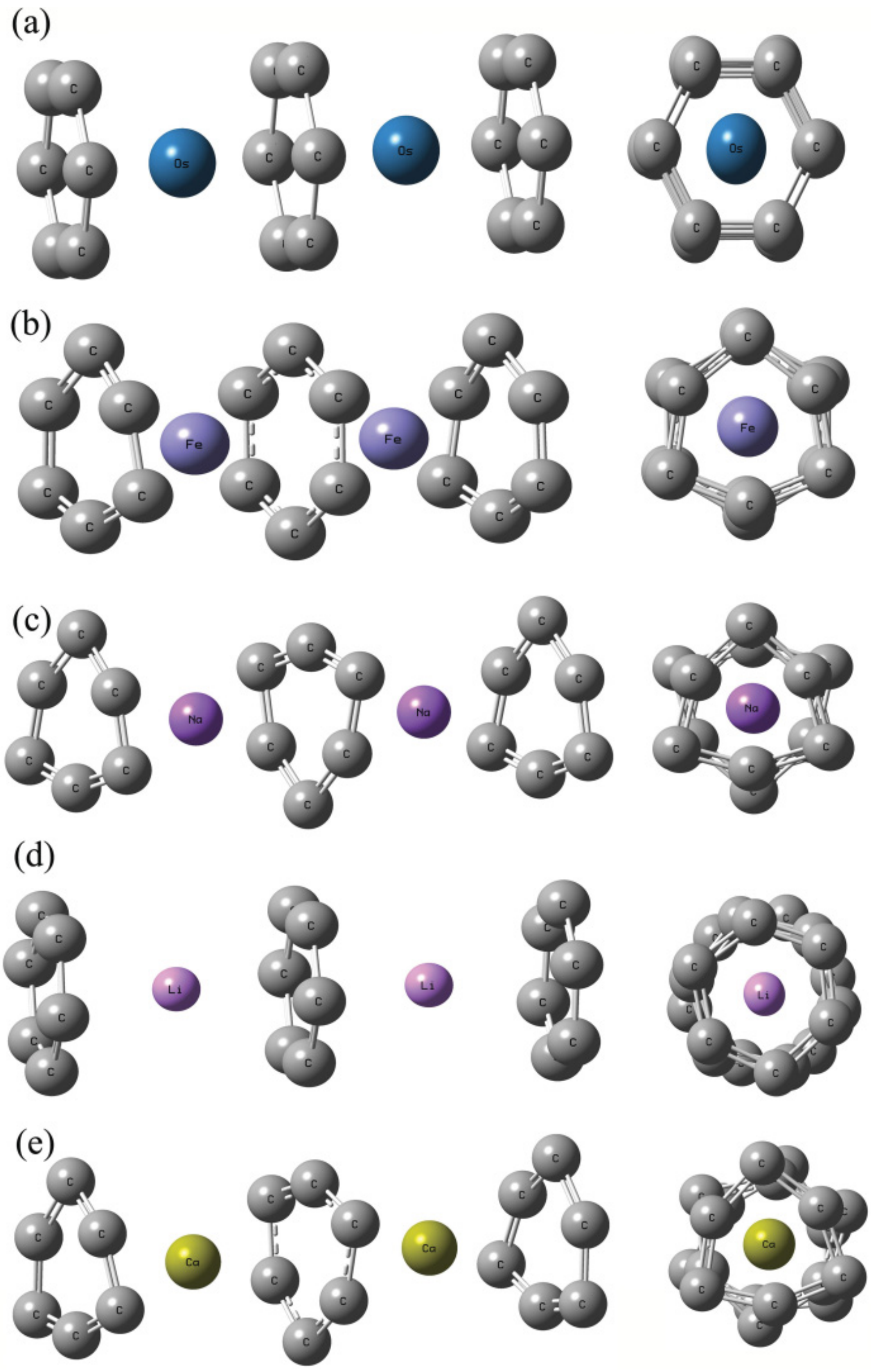

FIG. 1. (Color online) Examples of the different symmetries in sandwich molecules M-(cyclic C_6) for molecules $(C_6)_3M_2$: (a) D_{6h} symmetry in $(C_6)_3Os_2$ (b) D_{3h} symmetry in $(C_6)_3Fe_2$ (central ring with C_6 symmetry) (c) D_{3h} symmetry in $(C_6)_3Na_2$ (central ring with C_3 symmetry) (d) C_3 symmetry in $(C_6)_3Li_2$ (all rings with C_6 symmetry) and (e) C_{3h} symmetry in $(C_6)_3Ca_2$ (all rings with C_3 symmetry).

with the overall length of the molecule (Fig. 4) which shows calculated solutions for Rb and Fe compounds. It can be seen that the average bond energy does not change much in larger molecules, particularly for Rb compounds.

III. ELECTRONIC PROPERTIES

We can see from Table I that the HOMO-lowest unoccupied molecular orbital (LUMO) energy gap in most molecules is typically <1 eV, indicating that some of these molecules may be intrinsic conductors. The LUMO-HOMO gap vs. molecule length for $(C_6)_nFe_{n-1}$ is plotted in Fig. 5 and shows the tendency for this energy to approach 0.25 eV when n exceeds 5.

We show the bonding and orbital structure in $(C_6)_5Fe_4$ and $(C_6)_5Rb_4$ in Figs. 6 and 7, respectively. In $(C_6)_5Fe_4$ it is evident that the HOMO and LUMO orbitals correspond to two components of the same doubly degenerate energy level. This is very common feature of electronic structure of metal atoms and clusters. As electrons in these orbitals are highly delocalized, this provides further evidence that $(C_6)_5Fe_4$ should be conductive. On the other hand, in $(C_6)_5Rb_4$ (Fig. 7) the HOMO and LUMO orbitals and their neighboring orbitals are localized near certain carbon rings, which corresponds to the tight bonding electron model. This is a direct consequence of the presence of ionic bonding between individual metal atoms and carbon rings. As a result, although the energy gap in this molecule

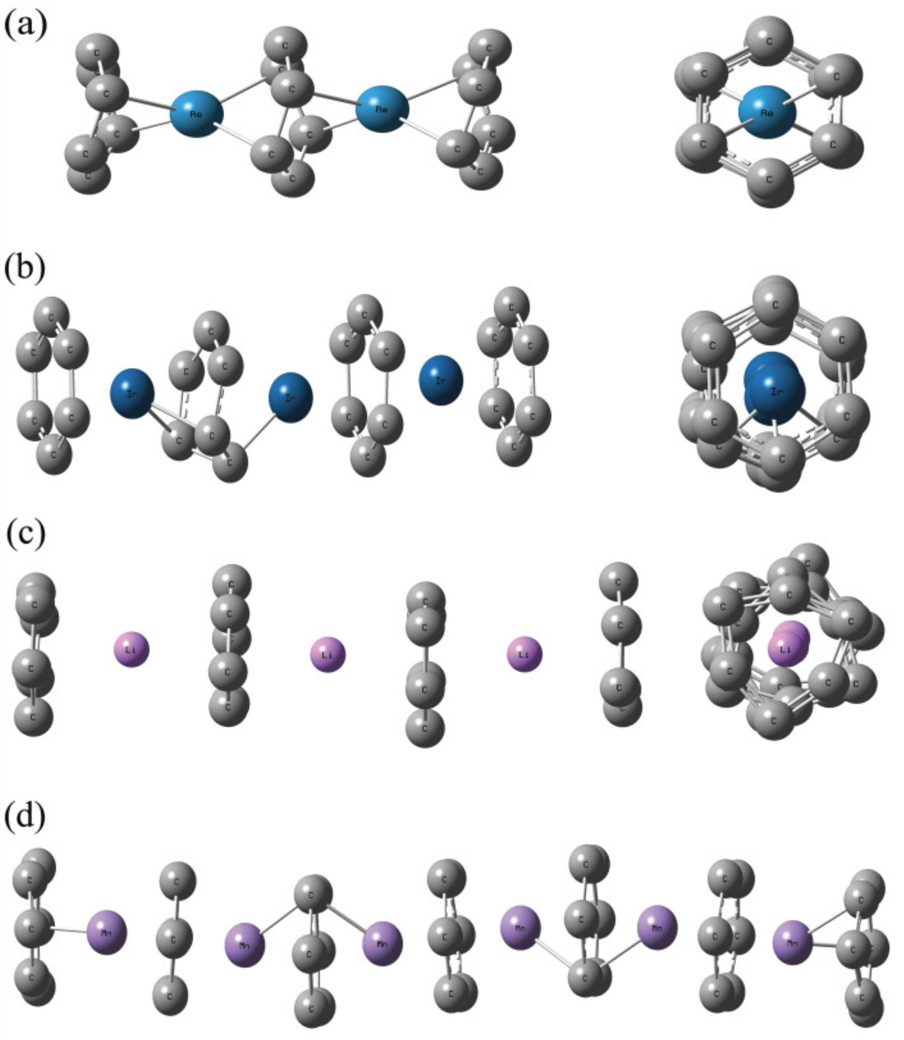

FIG. 2. (Color online) Structural distortion in sandwich molecules *M*-(cyclic C_6): (a) $(C_6)_3Re_2$, (b) $(C_6)_4Ir_3$, (c) $(C_6)_4Li_3$, and (d) $(C_6)_7Mn_6$.

TABLE II. Geometry and bond parameters for metal-organic molecules $(C_6)_nM_{n-1}$ with $n > 4$

Structure	Calculation method	Molecular symmetry	Average bond length between two cyclic C_6 (Å)	Average length of the bond in cyclic C_6 in the central ring (Å)	Average metal-C_6 bond energy (eV)	Average Mulliken charge on metal atom	Presence of structural distortion
$(C_6)_5Fe_4$	B3LYP/6-311G*	D_{6h}	3.18	1.41	12.5	0.832	
$(C_6)_5Li_4$	B3LYP/6-311G*	C_3	4.06	1.36	2.77	0.581	*
$(C_6)_5Ca_4$	B3LYP/6-31G*	C_3	4.84	1.4	10.79	0.982	*
$(C_6)_5Ba_4$	B3PW91/LANL2DZ	C_3	5.76	1.41	9.56	1.889	
$(C_6)_5Cs_4$	B3PW91/LANL2DZ	C_3	6.91	1.37	2.51	0.932	*
$(C_6)_5Rb_4$	B3PW91/LANL2DZ	Near D_{3h}	6.45	1.37	3.83	0.927	
$(C_6)_5Ru_4$	B3PW91/LANL2DZ	D_{6h}	3.56	1.46	12.46	0.949	
$(C_6)_5Tc_4$	B3PW91/LANL2DZ	D_{6h}	3.54	1.46	12.89	0.927	
$(C_6)_6Fe_5$	B3LYP/6-311G*	D_{6h}	3.17	1.41	16.05	0.835	
$(C_6)_6Os_5$	B3PW91/LANL2DZ	D_{6h}	3.54	1.47	29.14	0.982	*
$(C_6)_6Re_5$	B3PW91/LANL2DZ	D_{6h}	3.57	1.48	4.38	1	*
$(C_6)_7Fe_6$	B3LYP/6-311G*	D_{6h}	3.16	1.39	14.72	0.836	
$(C_6)_7Mn_6$	B3LYP/6-31G*	C_3	3.31	1.41	4.67	0.567	*
$(C_6)_7Ru_6$	B3PW91/LANL2DZ	D_{6h}	3.55	1.44	6.18	1.008	
$(C_6)_8Fe_7$	B3LYP/6-311G*	D_{3h}	3.16	1.41	9	0.834	

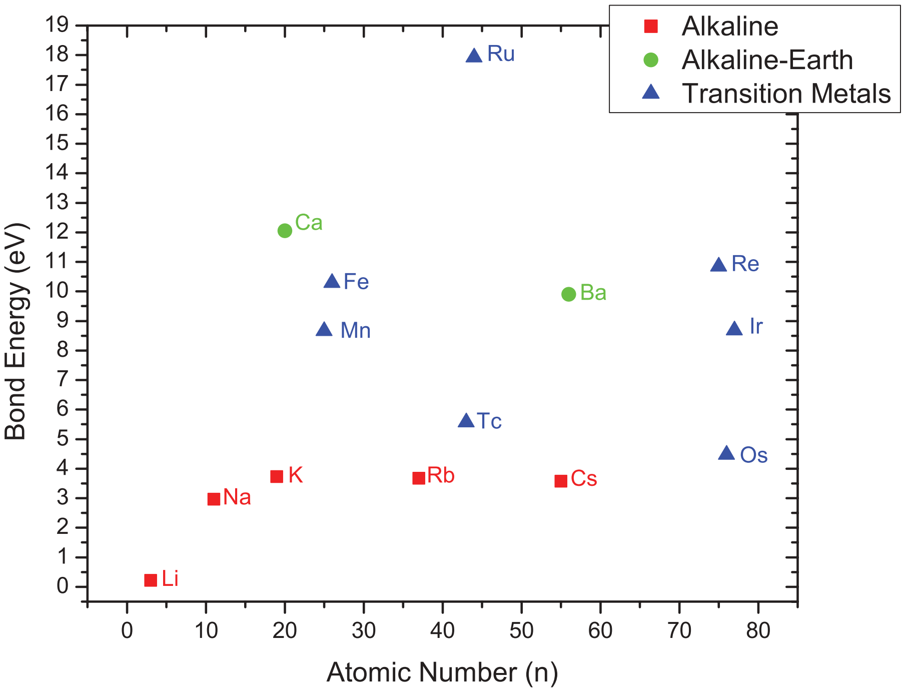

FIG. 3. (Color online) Average bond energy between the metal atom and cyclic C_6 in $(C_6)_3M_2$.

is very small (≈0.24 eV) and the difference in energy with neighbor energy level is approximately the same, conductivity is possible only by "hopping" of the electrons from one orbital to another. Additional calculations are required to evaluate the role of conduction in this molecule.

IV. MAGNETIC PROPERTIES

The magnetic properties of one-dimensional metal-organic sandwich wires analogous to $(C_6)_nM_{n-1}$ stacks have been the subject of many studies. Particular attention has been paid to magnetism in highly stable V-benzene sandwiches [19–21,23,33–35] and in poly-ferrocene sandwich clusters [22,34]. Theoretical calculations have been supported by laboratory studies [36,37] and demonstrate that metal-organic sandwich molecules containing the transition metals V, Fe, Ti, and Sc are all ferromagnetic. In all cases, the total molecular magnetic moment is determined by the sum of the atomic magnetic moments, orbital magnetic moments, and the spin-orbit interaction.

In 3*d* transition metal-organic sandwich molecules the atomic magnetic moment is determined by the number of uncoupled electrons in the 3*d* orbital shell [34]. For example, in M_nB_{n+1}, where M denotes transition metal and B benzene, the

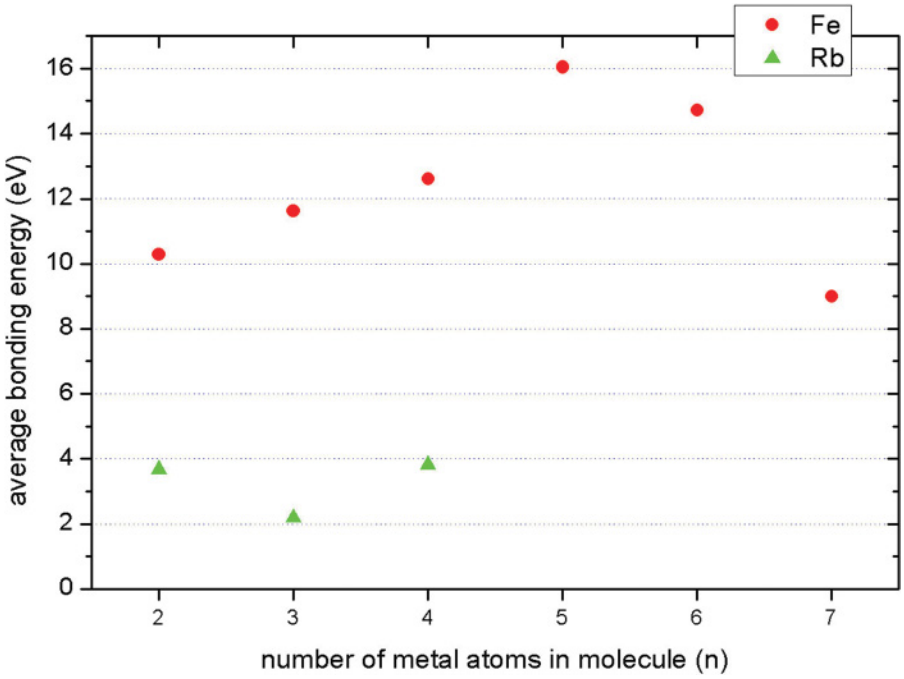

FIG. 4. (Color online) Dependence of the bond energy between the metal atom and cyclic C_6 in $(C_6)_nFe_{n-1}$ and $(C_6)_nRb_{n-1}$ vs. molecule length.

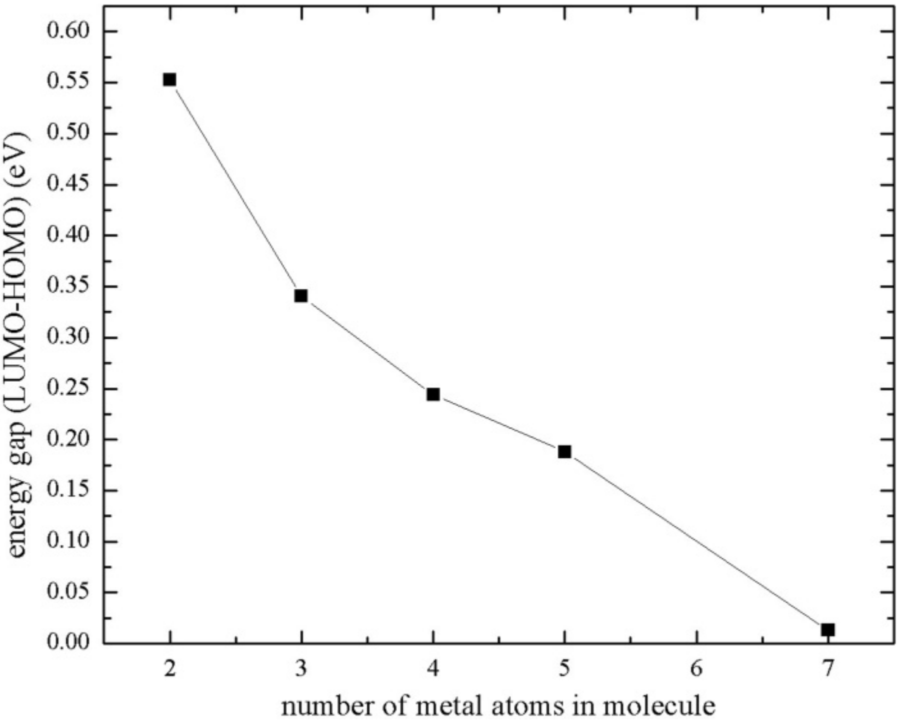

FIG. 5. (Color online) Dependence of the LUMO-HOMO energy gap vs. overall length in $(C_6)_n Fe_{n-1}$.

number of uncoupled 3d electrons for V, Ti, and Sc is $n = 1$, 2, and 1, respectively, and the maximum magnetization in these atoms $\mu_Z = 1$, 2, and 1 respectively (in Bohr magneton units). The calculated total magnetic moment of the unit cell of the polymer molecule with V, Ti, and Sc atoms is, however, 0.88, 1.0, 0.5 μ_B, respectively [33,34]. The reduction of the total

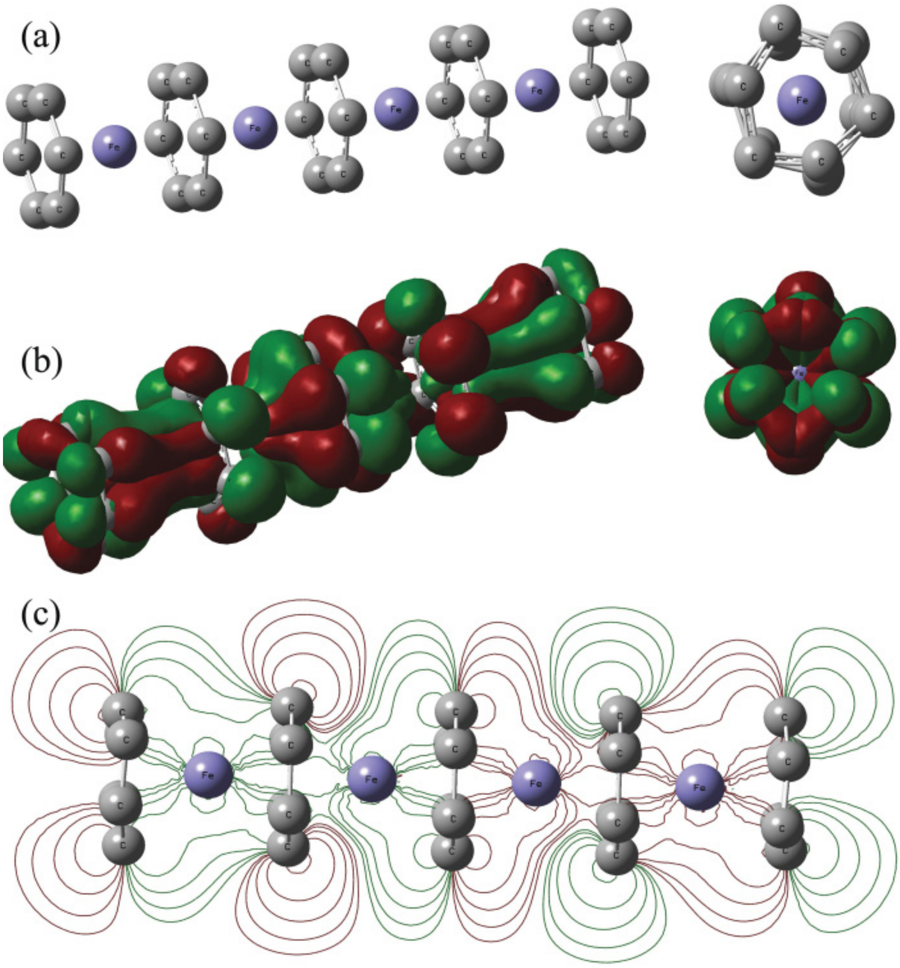

FIG. 6. (Color online) Structure of $(C_6)_5Fe_4$ and its degenerate combined HOMO-LUMO orbital (AO 142-143). (a) Structure, (b) combined HOMO-LUMO orbital (AO 142-143), and (c) electron density distribution in the combined HOMO-LUMO orbital.

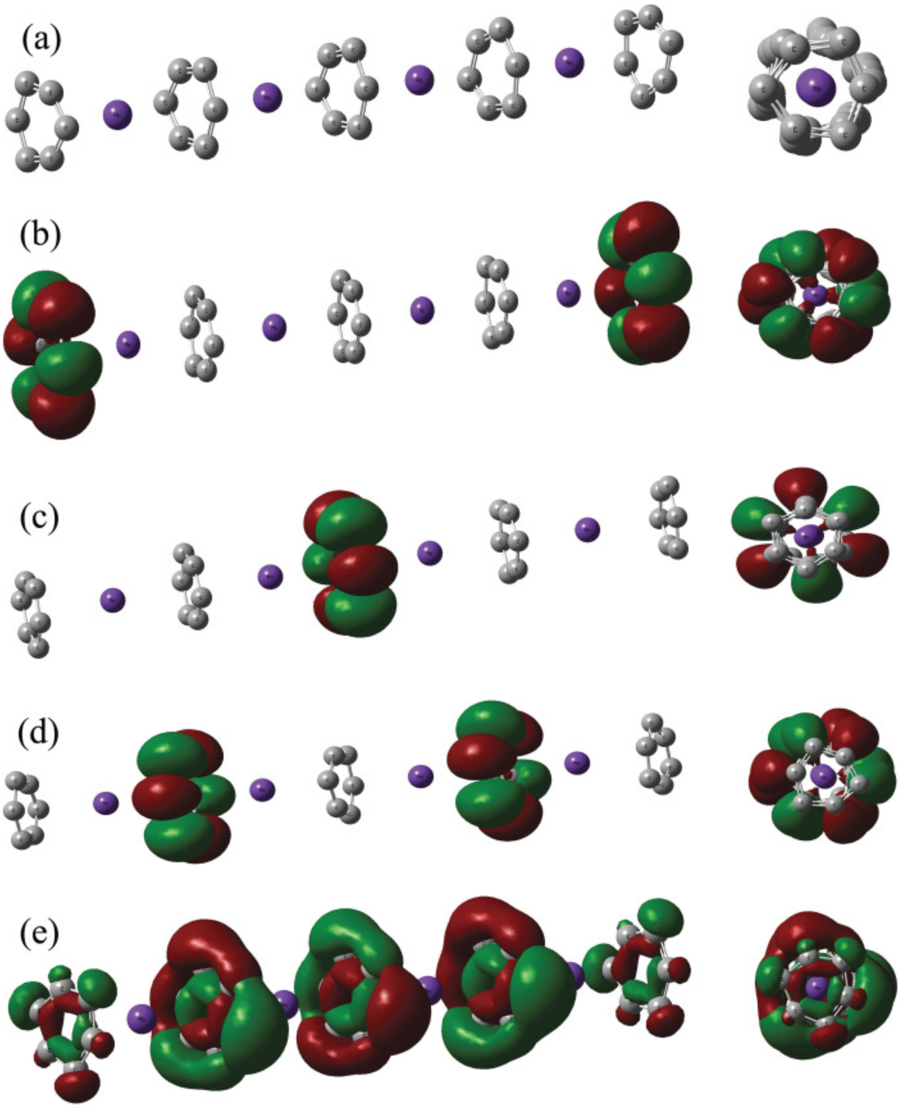

FIG. 7. (Color online) Structure and some of the atomic orbitals in $(C_6)_5Rb_4$: (a) structure, (b) combined degenerate orbital (AO166-167), (c) LUMO (AO165), (d) combined degenerate HOMO (AO163-164), and (e) combined degenerate orbital (AO160-162).

magnetic moment is attributable to the spin-orbit interaction [20]. As a result of this term, each benzene ring acquires a small negative magnetic moment along the molecular axis. This is typically $\approx 0.15\ \mu_B$ [21]. Another mechanism for reduction of the molecular magnetic moment involves intra-spin-relaxation (ISR) effects [37]. For molecules like V_2B_3, V_3B_4, and V_5B_6 experiments [36,37] show that the magnetic moments per unit cell are 0.75, 0.77, and 0.72, respectively.

A comparative analysis of the magnetic properties of magnetization in 3*d* and some 4*d* transition-metal M_nB_{n+1} compounds and in polyferrocene molecules has been published by Shen *et al.* [34]. In $Fe_n(C_5H_5)_n$ the magnetic moment was found to be μ_B per Fe atom and the total magnetic moment of these molecules is found to be proportional to the number of metal atoms.

These results can be used to predict some magnetic properties of $(C_6)_nM_{n-1}$ sandwich molecules based on multiple layers of cyclic C_6 and are closest in composition to polyferrocene structures. Of most interest is magnetization in compounds such as $(C_6)_nFe_{n-1}$ which represent the most stable stacked C_6 clusters. From Tables I and II it is apparent that the Mulliken electric charge of the transition metals atoms in these molecules is nearly unity. This implies that one valence electron of the metal atom participate the chemical bond between metal and cyclic C_6. This is similar to the situation in long polyferrocene molecules where C_5H_5 accepts an electron from the Fe atom. The magnetic moment of the ion Fe^+ is μ_B so $(C_6)_nFe_{n-1}$ has a total magnetic moment of $\approx\mu_B$ per molecular unit cell. In general, the magnetic moment of $(C_6)_nM_{n-1}$ is determined both by the moment of the metal and that resulting from the electron transferred to the cyclic C_6 ring. By inference from the properties of M_nB_{n+1}, the magnetic moment arising from each cyclic C_6 ring is then expected to be $(0.1\text{–}0.3)\mu_B$. We then expect that the Fe spins in $(C_6)_nFe_{n-1}$ will be aligned ferromagnetically while those in cyclic C_6 in will have an antiferromagnetic configuration. As a result, the total magnetic moment in $(C_6)_nFe_{n-1}$ is expected to be $(0.7\text{–}0.8)\mu_B$ per unit cell.

V. CONCLUSIONS

We have used first-principles techniques to investigate the structure and electronic properties of metal-carbon sandwich molecules formed by cyclic C_6 rings with intercalated metal atoms. We find that these structures are quite stable with metal-ring bond energies exceeding 11.6 eV in larger molecules. The types of metal atoms that can be incorporated in these molecules form two groups. One of these involves the alkali metals and some of the alkaline earth metals, while the other consists of several transition metals. A unique property of a number of these MC_6 sandwich molecules is that the units repeat on a periodic basis. The most stable compounds are indicated to be $(C_6)_5Fe_4$ and $(C_6)_5Rb_4$. We find that the M-C_6 ring bond energy in $(C_6)_nFe_{n-1}$ and $(C_6)_nRb_{n-1}$ increases with the length of these molecules up to a limiting value suggesting that it may be possible to form long polymer molecules from these compounds. In general, this type of structure constitutes the molecular analog of intercalated graphite. As a result, these compounds may possess interesting properties as molecular conductors and superconductors.

ACKNOWLEDGMENTS

This work was supported by NSERC and was made possible by the facilities of the Shared Hierarchical Academic Research Computing Network (SHARCNET).

---

[1] J. M. L. Martin, J. P. Francois, and R. Gijbelst, J. Comp. Chem. **12**, 52 (1991).
[2] K. Raghavachari, R. A. Whiteside, and J. A. Pople, J. Chem. Phys. **85**, 6623 (1986).
[3] T. Torelli and L. Mitas, Phys. Rev. Lett. **85**, 1702 (2000).
[4] J. Hutter, H.-P. Luethi, and F. Diederich, J. Am. Chem. Soc. **115**, 750 (1994).
[5] F. Grein, J. Franz, M. Hanrath, and S. D. Peyerimhoff, Chem. Phys. **263**, 55 (2001).
[6] J. M. L. Martin, J. El-Yazal, and J.-P. François, Chem. Phys. Lett. **242**, 570 (1995).
[7] J. M. L. Martin and P. R. Taylor, J. Phys. Chem. **100**, 6047 (1996).
[8] J. Haubrich, M. Muehlhaeuser, and S. D. Peyerimhoff, Phys. Chem. Chem. Phys. **4**, 2891 (2002).
[9] H. Masso and M. L. Senent, J. Phys. Chem. A **113**, 12404 (2009).
[10] Ying Xu, Li-Ling Zhou, and Z. X. Dai, Phys. Lett. A **372**, 4465 (2008).
[11] W. Weltner, K. R. Thompson, and R. L. DeKock, J. Am. Chem. Soc. **93**, 4688 (1971).
[12] J. Fulara, E. Riaplov, A. Batalov, I. Shnitko, and J. P. Maier, J. Chem. Phys. **120**, 7520 (2004).
[13] J. D. Presilla-Marquez, J. A. Sheehy, J. D. Mills, P. G. Carrick, and C. W. Larson, Chem. Phys. Lett. **274**, 439 (1997).
[14] S. L. Wang, C. M. L. Rittby, and W. R. M. Graham, J. Chem. Phys. **107**, 6032 (1997).
[15] Stanislav Kuzmin and Walter W. Duley, Phys. Lett. A **374**, 1374 (2010).
[16] Sakir Erkoc, J. Mol. Struct., Theochem. **639**, 157 (2003).
[17] O. B. Malcioglu and S. Erkoc, J. Mol. Graphics Modell. **24**, 213 (2005).
[18] K. Hoshino *et al.*, J. Phys. Chem. **99**, 3053 (1995).
[19] T. Yasuike and S. Yabushita, J. Phys. Chem. A **103**, 4533 (1999).
[20] Y. Mokrousov *et al.*, Nanotechnology **18**, 495402 (2007).
[21] J. Wang, P. H. Acioli, and J. Jellinek, J. Am. Chem. Soc. **127**, 2812 (2005).
[22] S. Nagao, A. Kato, and A. Nakajima, J. Am. Chem. Soc. **122**, 4221 (2000).
[23] R. Pandy *et al.*, J. Am. Chem. Soc. **123**, 3799 (2001).
[24] T. Yasuike *et al.*, J. Phys. Chem. A **101**, 5360 (1997).
[25] M. Mitsui *et al.*, J. Phys. Chem. Lett. B **110**, 2968 (2006).
[26] Tsuyoshi Kurikawa *et al.*, Organometallics **18**, 1430 (1999).
[27] S. Nagaoka *et al.*, Eur. Phys. J. D **52**, 103 (2009).
[28] X. L. Wang, M. Y. Ni, and Z. Zeng, e-print arXiv:1002.4323v1 [cond-mat.mtrl-sci].
[29] H. Xiang, J. Yang, J. G. Hou, and Q. Zhu, J. Am. Chem. Soc. **128**, 2310 (2006).
[30] M. J. Frisch *et al.*, GAUSSIAN, Inc., Wallingford CT (2004).
[31] J. T. Lyon and L. Andrews, J. Phys. Chem. A **109**, 431 (2005).
[32] J. Kua and K. M. Tomlin, J. Phys. Chem. A **110**, 11988 (2006).
[33] A. Goto and S. Yabushita, Chem. Phys. Lett. **454**, 382 (2008).
[34] L. Shen *et al.*, J. Am. Chem. Soc. **130**, 13956 (2008).
[35] H. Weng, T. Ozaki, and K. Terakura, Phys. Rev. B **79**, 235118 (2009).
[36] K. Miyajima, A. Nakajima, S. Yabushita, M. B. Knickelbein, and K. Kaya, J. Am. Chem. Soc. **126**, 13202 (2004).
[37] K. Miyajima, S. Yabushita, M. B. Knickelbein, and A. Nakajima, J. Am. Chem. Soc. **129**, 8473 (2007).