

Metallocarbohedrenes: A New Class of Metal–Carbon Assemblies

B. V. Reddy and S. N. Khanna*

Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000

Received: May 31, 1994; In Final Form: June 20, 1994*

The electronic structure and stability of metallocarbohedrenes (met-car) and cubic structures containing Ti and C or N have been studied using the ab-initio density functional approach. We show that while the met-car and the cubic structures have comparable binding energies per atom for the case of carbides, the cubic structures are more stable for metal–nitrogen systems. This change in behavior is shown to be related to the differences in the nature of electronic bonds which stabilize the two structures. By studying small Ti_nC_m and Ti_nN_m ($n + m < 6$) clusters, we identify these electronic features and show that the met-car and cubic arrangements represent two different families whose formation is governed by the composition of the beam.

Introduction

Ever since the discovery of C_{60} and the associated fullerene materials,¹ there has been a constant search for new very stable clusters.^{2,3} One way to proceed is to use the fact that clusters are small fragments of the bulk, and therefore very stable solids should have very stable clusters. Refractory transition metal carbides and nitrides fall in this category since they are highly stable as evidenced by large cohesive energies and very high melting points. Most of them crystallize in a “MX” ($M = Ti, V, Zr$, etc.; $X = C, N$) phase with a face-centered NaCl structure and are marked by strong covalent (partially ionic) bonds between the transition metal and carbon (nitrogen) atoms. There is practically no bonding between either transition metal or carbon (nitrogen) atoms.⁴ Further, the MX phases show marked deviations from stoichiometry. These features make their clusters where topology and composition can be varied over a wide range as a potential candidate for the new search.

About 2 years ago, Castleman and co-workers³ produced Ti_nC_m clusters in molecular beams by reacting transition metal vapors with a variety of hydrocarbons. The ensuing mass spectrum showed a marked peak which was identified, by isotopic substitution, to correspond to a 20-atom cluster composed of 8 Ti and 12 C atoms. To probe its structure, Castleman et al. used the selective chemical reactivity of the transition metal atoms with H_2O and ND_3 , and on the basis of these reactions they proposed a caged dodecahedral structure (Figure 1a) composed of 12 pentagons. Each pentagon had a C_2 as a base, a C at the apex, and the two Ti occupying the remaining farther sites. Subsequent theoretical investigations⁵ confirmed that the cluster indeed had a high binding energy of about 6.5 eV/atom although the original structure is recently proposed⁶ to undergo substantial Jahn–Teller distortions which enhance its binding by several electronvolts. The new cluster called the metallocarbohedrene (met-car) was proposed to have important applications in electronic materials, pollution tracers, etc.

The discovery of a highly stable 20-atom cluster with a Ti:C ratio of 1:1.5 is intriguing since the bulk phase has a 1:1 composition. Even if the stability of the cluster could be reconciled with the high stability of TiC bulk, the existence of nondissociated C_2 molecules and the cage structure are both unusual since the bulk has a compact structure with dissociated C atoms. Further, the original beams did not contain any clusters which would correspond to bulk fcc fragments. Recent

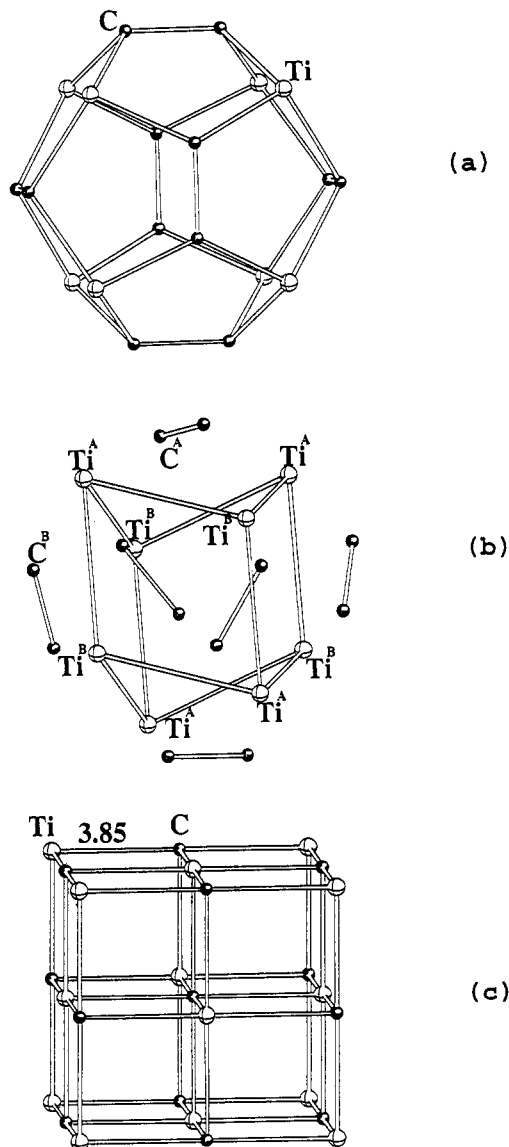


Figure 1. (a) Dodecahedral structure of a Ti_8C_{12} cluster. (b) The new caged structure of a Ti_8C_{12} cluster. The different Ti or C sites have been labeled as A or B. (c) A 27-atom fcc cluster containing 14 Ti and 13 C atoms.

experiments,⁷ however, not only produce both the met-car and the cubic units but also can switch between the two structures⁸ by controlling experimental conditions. A further surprise came

* Abstract published in *Advance ACS Abstracts*, August 1, 1994.

when the experimental group tried to make similar clusters containing titanium and nitrogen instead of carbon. The ensuing Ti_nN_m clusters⁹ were all found to correspond to cubic fcc compact fragments. Since a N_2 molecule has a higher binding energy than a C_2 molecule, it is not clear why met-cars which rely on C_2 molecular units for stability are not observed for the stronger N_2 molecule.

The above experiments raise several questions. (1) What are the relative stabilities of the cubic and the met-car structures in carbides and nitrides? (2) What are the electronic bondings which characterize the met-car and the cubic arrangements, and do the met-cars represent a new family of metal-carbon structures? Further, why do the metal-carbon systems prefer met-cars while the metal-nitrogen clusters favor cubic structures? (3) Can the source conditions affect the formation of met-cars or cubic structures in the case of carbides?

In this article we have carried out ab-initio density functional studies on Ti_nC_m and Ti_nN_m clusters to resolve the above issues. Our studies based on the cubic $Ti_{14}C_{13}$ and the new Ti_8C_{12} met-car structures show that they have comparable binding energies per atom and hence should be observable provided the experimental conditions permitted their formation. The corresponding calculations on Ti_8N_{12} and $Ti_{14}N_{13}$ clusters, however, show the cubic fragments to be more stable than met-cars. To provide an insight to this difference in behavior, we then present model studies on small Ti_nC_m and Ti_nN_m ($n + m < 6$) clusters. They indicate that the met-cars are a new family of Ti-X ($X = C, N$) clusters marked by TiX and X_2^- bonds. Their stability for metal-carbon systems stems from the fact that C_2^- is more stable than C_2 . For nitrogen, on the other hand, N_2^- is less stable than N_2 , making them less favorable compared to cubic structures. We would like to add that in a recent paper¹⁰ we had investigated the relative stability of met-cars and cubic structures for metal-carbon systems using the dodecahedral structure. Since the new met-car structure is more stable than the dodecahedral structure by as much as 11 eV, we offer, in this work, a reinvestigation of the issue.

Details of Calculations

All our theoretical studies have been carried out using a linear combination of atomic orbitals molecular orbital approach.¹¹ The exchange correlation effects have been built through the use of local density approximation. Our studies employed two complementary schemes which differ in the nature of basis functions used to expand the molecular orbitals. In the first scheme,¹² usually referred to as the linear combination of Gaussian type orbitals (LCGTO), uncontracted Gaussians were used as basis functions. In this version, we used nonlocal pseudopotentials¹³ to replace the deep cores. The basis sets consisted of 5s, 2p, and 4d Gaussians for Ti and 5s and 4p Gaussians for N or C when studying smaller clusters. For met-cars, the basis set for Ti contained 5s, 1p, and 3d Gaussians. The charge density and the exchange correlation potential and energy were fitted by Gaussians centered at the atomic sites and in between the bonds. For details, the reader is referred to earlier papers.¹² In the alternate scheme, usually called the discrete variational method (DVM),¹⁴ atomic orbitals calculated by solving radial atomic equation on a mesh of points were used to expand the molecular functions. Here the matrix elements entering the Kohn-Sham equations were calculated numerically by integrating on a mesh of points. In this scheme we used $3d^{2.4}s^{1.99}4p^{0.01}$ atomic orbitals for Ti, $2s^{2.2}2p^3$ for N, and $2s^{2.2}2p^2$ for C. Our experience shows that while the DVM permits studies on larger systems, and does permit reliable estimates of relative stability, the absolute binding energies can have variations. On the other hand, the LCGTO

TABLE 1: Bond Lengths (au) and Binding Energy (BE, eV/atom) of the New Cage Structure of Ti_8C_{12} Cluster^a

parameter	DVM	LCGTO	parameter	DVM	LCGTO
C^A-C^A	2.73	2.56	Ti^A-C^B	3.69	3.68
C^B-C^B	2.73	2.64	Ti^B-C^A	3.79	3.77
Ti^A-Ti^B-H	5.27	5.18	Ti^B-C^B	4.04	3.90
Ti^B-Ti^A-V	5.27	5.24	BE	6.7	7.1
Ti^A-C^A	4.03	3.88			

^a H and V correspond to nearly horizontal and vertical Ti-Ti bonds.

is computer intensive but the energies are very accurate. One is, however, restricted to smaller sizes. In this work, we have used DVM for larger clusters and LCGTO for smaller clusters. To provide an estimate of the effect of basis functions and other approximations, we also present results on intermediate clusters using both methods.

Results and Discussion

We start by considering the structure of the met-cars. In an earlier paper,⁵ we had presented our studies on the dodecahedral structure originally proposed by Castleman et al.³ This structure shown in Figure 1a can be looked upon as a cube of Ti atoms with faces decorated by six C_2 molecules. In a subsequent paper,¹⁰ we had also shown that the binding energy was enhanced by distortions which would increase the number of TiC bonds. We had therefore conceived a structure where two of the C_2 molecules were oriented to bond with three Ti sites. In a recent paper, Chen et al.⁶ have suggested a structure which further maximizes the TiC bonds by distorting the Ti cube. This structure for our calculated bond lengths is shown in Figure 1b. Note that there are two sets of nonequivalent Ti and C sites which are labeled as Ti^A , Ti^B , C^A , and C^B . We find this cluster to be about 11 eV (in DVM) more stable than the dodecahedral structure. In Table 1 we give our calculated bond lengths and binding energy. They are close to those obtained by other calculations.⁶ A Mulliken population analysis shows that both types of Ti sites lose nearly 1 e^- whereas the C sites gain about 0.7 e^- . The C_2 molecules are therefore in an anionic state.

We now consider the stability of met-car vis-à-vis the corresponding bulk fragment. For this part of our work, we chose a 27-atom cluster shown in Figure 1c. The TiC bond length was varied to minimize the energy. Using DVM, we find that the cluster has a binding energy of 6.7 eV/atom. Note that in these studies only the TiC bond length was optimized. A complete optimization allowing all structural distortions is extremely difficult using the present computational resources. We therefore studied smaller clusters (Ti_6C_6) where we allowed structural distortions. The gain in binding energy was less than 0.15 eV/atom. We also investigated any effects arising due to differences in size since a met-car has 20 atoms while $Ti_{13}C_{14}$ has 27 atoms. For Ti_6C_6 and Ti_9C_9 our calculations gave a binding energy of 6.3 and 6.6 eV/atom, respectively, compared to 6.7 eV/atom for 27-atom cluster. Within the accuracy of DVM, the binding energy of a cubic cluster is therefore comparable to the corresponding DVM value of 6.7 eV/atom for a met-car, making them equally stable. We found that the Ti sites donate between 0.92 and 1.2 e^- 's depending on their location. This is nearly the same as in case of met-cars, but the C sites gain 1.1–1.3 e^- 's as opposed to 0.7 e^- in met-cars due to different compositions. There are no C-C bonds, and the cluster is almost entirely stabilized by TiC bonds.

The above results show that Ti and C atoms can form two nearly equally stable clusters. The met-car is stabilized by TiC and C_2 units while the cubic structure only has TiC bonds with

nearly no C—C bonding. The question arises as to why the two structures are not observed in all experiments. Further, why do C atoms exist as C_2 molecules in met-cars and dissociated atoms in cubic structures? Before we answer these questions, let us consider the case of nitrides. The fact that N_2 is stronger than C_2 would suggest that the nitrogen met-cars should be more stable than cubic structures. To examine this, we calculated the binding energy of the met-car and the fcc unit by replacing the C by N atoms. Surprisingly, the met-car was less stable with a binding energy of 4.2 eV/atom (5.9 eV/atom using LCGTO) as opposed to fcc structure which had 5.1 eV/atom in the DVM calculations. This result is in perfect agreement with experiments⁹ which do observe only cubic structures for nitrides. However, the reduced stability of met-cars vis-à-vis the cubic structure in the case of nitrogen does pose a puzzle.

To provide insight in to the above results, we now consider the nature of bonding in small Ti_nC_m and Ti_nN_m clusters. In particular, we focus on the effect of Ti composition on the C_2 and N_2 bonds. For this part of our work, we have used the LCGTO code. The highest occupied atomic orbital (HOMO) in Ti is 4 eV higher than the HOMO in C and 6.2 eV higher than in N. This suggests that any bonding between Ti and C or N will involve charge transfer from Ti to N or C. With this in mind, we first studied neutral and anionic C_2 and N_2 molecules. For C_2 , C_2^- , N_2 , and N_2^- we obtain binding energies of 6.6, 10.4, 9.5, and 8.0 eV and bond lengths of 2.34, 2.40, 2.13, and 2.33 au, respectively. Note that while C_2^- is more stable than C_2 , N_2^- is less stable than N_2 . In Figure 2 we show our calculated geometries of the Ti_nC_m ($n + m < 6$) clusters. For TiC our calculated binding energy of 4.5 eV is comparable to the experimental value of 4.38 eV.¹⁵ For TiC_2 we obtain a triangular configuration with a C—C bond length of 2.5 au. A charge density analysis indicates it to be an anionic C_2 molecule bound to Ti. Further addition of a Ti atom leads to a Ti_2C_2 cluster with 1:1 composition. Its geometry was optimized by assuming a C_2 and Ti_2 molecules perpendicular to each other and varying the C—C, Ti—Ti, and the separation between their centers to minimize the energy. The ground state is a nearly square configuration with no bonding between the C atoms as in bulk TiC. We then added an extra C atom at the apex and started with a geometry with a base C—C, Ti—Ti at a height h , and the C atoms at a height l . This geometry was motivated by the pentagons decorating the faces of the dodecahedral structure (Figure 1a). The C—C and Ti—Ti bond lengths and the heights h and l were optimized. A similar structure but with Ti—Ti in the same plane as three C atoms had a lower binding energy. What was most interesting was that the C atoms forming the base had a separation of 2.40 au, close to a C_2 molecule. The above results demonstrate an interesting progression in the nature of C—C bonding. For a Ti:C ratio of 1:1 as in Ti_2C_2 , the C atoms appear as dissociated atoms. On the other hand, for a C to Ti ratio of 1.5 and more, the C—C bonds persist. This progression in bonding can be understood in terms of the energetics of TiC and C_2^- bonds. We found that the Ti—C bonding occurs primarily via an interaction of Ti d (xy) orbital and C p orbitals. If this d—p mixing was the only interaction, the C atoms would bind with a C—Ti—C angle of 90°. However, a C_2 molecule can also enhance its binding by forming C_2^- . There is, thus, an interplay between optimal dp and anion formation. A TiC_2 has two TiC and one C_2 bond. The binding energy of C_2^- is greater than twice that of TiC, forcing it to be a negative C_2 molecule bound to a Ti. For Ti_2C_2 , however, the preponderance of TiC bonds over a single C_2 bond forces optimal pd mixing with a squarish configuration. This enhanced

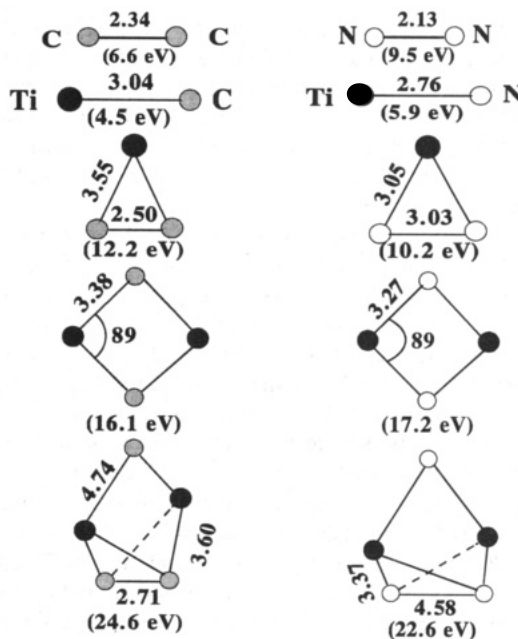


Figure 2. Ground state geometry and binding energies of C_2 , TiC, TiC_2 , Ti_2C_2 , Ti_2C_3 , N_2 , TiN, TiN_2 , Ti_2N_2 , and Ti_2N_3 clusters. The bond lengths are in atomic units (au) and the energies in electronvolts.

pd mixing was also reflected in the increased Mulliken charge per C atom. The situation again changes for Ti_2C_3 where the central Ti's prefer to bind with top C and the lower C's restore a C_2 bond. In general, for low Ti content, the number of possible TiC bonds is smaller and the clusters favor configurations with C_2^- like bonding, while for Ti—C compositions approaching 1:1, the TiC binding dominates and favors dissociated C atoms. This really brings out the basic difference between met-cars and the cubic structures. The met-cars, because of their Ti:C composition, are a new phase stabilized by C_2^- like and less than optimal Ti—C bonds. The cubic phase is a different phase marked by dissociated C atoms and stabilized by TiC bonds. Both clusters, however, have comparable binding energies, but their formation depends on the experimental conditions. Beams rich in Ti (low in C) would prefer cubic structures, while in Ti-poor (C-rich) situations, the met-cars would prevail.⁸

We now discuss the case of nitrides. In Figure 2 we also show the geometries of Ti_nN_m clusters. For Ti_2N_3 we have only examined geometries similar to Ti_2C_3 , and the structure in Figure 2 may not be the final ground state. Our objective here is to compare the behavior of C and N in similar situations. For TiN_2 , we find a N—N separation of 3.03 au, which is considerably larger than 2.13 au for a neutral N_2 . The N—N bond is therefore stretched as opposed to C_2 bond in TiC_2 . This difference arises because (1) N_2^- is less stable than N_2 and (2) TiN is stronger than TiC. The stability obtained by forming anionic species in the case of C is therefore absent for nitrides. In fact, TiN_2 is very unstable; e.g., it takes only 0.66 eV to break a TiN_2 in to Ti and N_2 . The larger Ti_nN_m clusters also have weakened or broken N—N bonds. Therefore, the Ti_nN_m clusters do not stabilize by forming N_2^- bonds as is the case for the carbides and prefer cubic structures stabilized by TiN.

Conclusions

To summarize, we have shown that met-cars represent a new family of metal—carbon systems different from the bulk phase. For metal—carbon systems the met-car and the fcc families have comparable stability, and their formation is governed by

experimental conditions. On the other hand, the nitrides favor cubic arrangements. The differences between nitrides and carbides are rooted in the stability of C_2^- , N_2^- , TiC , and TiN clusters. In view of these results, it will be interesting to examine the structure of clusters containing both carbon and nitrogen, e.g., say TiN_4C_8 . This will be discussed in a forthcoming paper.

Acknowledgment. The authors are grateful to Prof. A. W. Castleman, Jr., for discussions. This work was supported in part by a grant from the U.S. Department of Energy (Grant DE-FG05-87ER45316).

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