# Electronic Structure and Bonding in the Metallocarbohedrene $Ti_8C_{12}$

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Total-energy and electronic-structure calculations are presented for a recently proposed dodeca-hedral cluster of eight titanium and twelve carbon atoms. The calculations were done using density-functional theory and a cluster full-potential linear muffin-tin orbital method which is suited to arbitrary geometries and permits direct evaluation of the forces. As in the $C_{60}$ molecule, the atoms form a spherical graphitelike shell with a threefold coordination at all sites. The calculated C-C and Ti-C bond lengths are 2.63 and 3.76 bohrs; the binding energy is 6.6 eV per atom. The bonding mechanism is quite different from that of the graphite crystal or the $C_{60}$ molecule.

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Since the first observation of the $C_{60}$ molecule [1], much effort has been invested in the study of this novel molecular cluster. In $C_{60}$, the carbon atoms form a hollow sphere consisting of fivefold and sixfold rings, whereby each atom has a coordination number of three. It can be considered a spherical form of graphite and it has been shown that the bonding mechanism is essentially the same. A short time ago, Guo, Kerns, and Castleman [2] discovered an unusually stable charged cluster with the stoichiometry $Ti_8C_{12}$. Furthermore, they were able to show that the eight Ti atoms are similarly coordinated. Later, analogous molecules with Hf, Zr, or V in place of Ti were identified [3,4]. For neutral and ionized molecules of this type (named metallocarbohedrenes) they proposed the structure displayed in Fig. 1. The atoms are arranged at the corners of a dodecahedron with six $C_2$ dimers alternating with the eight Ti atoms. As in $C_{60}$, all atoms in this "soccerball-shaped" molecule are threefold coordinated; however, here only fivefold rings occur. Furthermore, the surface is more strongly curved and consequently the corresponding fullerene $C_{20}$ is not stable. Interestingly, Ti can form a metastable $\omega$



FIG. 1.   Dodecahedral structure of the $Ti_8C_{12}$ molecule, as proposed in Ref. [2], shown here with the relaxed bond lengths obtained from the present calculation.

phase which has been interpreted as partly covalent [5]. The question thus arises whether the proposed structure is correct and, if yes, to what extent the bonding mechanism in this carbon-titanium molecule is analogous to that in the carbon fullerenes, as suggested in Ref. [2]. To shed light on this question, we have performed *ab initio* electronic structure calculations for $Ti_8C_{12}$ in the proposed geometry. The results confirm the structure, whereby the dodecahedron is deformed somewhat due to the different lengths of C-C and Ti-C bonds. By studying the electronic wave functions and the charge density, we have analyzed the bonding. We find that the electronic structure can be understood as $C_2$ molecular orbitals combining with the Ti $d$ orbitals to make bonding cluster states. The Fermi energy lies between the bonding and nonbonding states, explaining the stability of the cluster. Contrary to previous expectations, no analog to the graphitic bonding in the $C_{60}$ molecule is found, showing that indeed $Ti_8C_{12}$ is a member of a new class of molecular clusters.

The calculations were done using a recently developed full-potential linear muffin-tin orbital (FP-LMTO) method which is designed for clusters, to be presented in detail elsewhere [6]. The basis for the representation of the electronic eigenstates consists of atom-centered spherical Hankel functions which are augmented by numerical solutions of the radial Schrödinger equation inside nonoverlapping atomic spheres. The combination of the augmentation technique with the use of LCAO-like atom-centered envelope functions leads to a very efficient basis set which can be applied to heavy and light elements equally well. As has been discussed previously [7], the main difficulty for a full-potential method using this basis set is to find a usable representation for the product of two such functions in the interstitial region (between the atomic spheres). As before, we represent these products as linear combinations of other atom-centered Hankel functions. In the new method, we first obtain an arbitrarily accurate representation for pairs of atoms
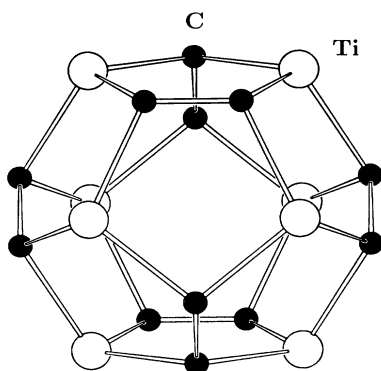
arranged along the $z$ axis. The expansion coefficients are tabulated as a function of the interatomic distance. For any other geometry, we obtain the needed expansion rapidly by evaluating the tabulated fit and applying rotation matrices. The electron-electron interaction is treated by the local-density approximation (LDA) [8, 9] within density-functional theory; hereby the interstitial exchange-correlation quantities are obtained by numerical integration. In addition, it has been possible to derive an exact and practicable force theorem within this technique. In sum, the applied FP-LMTO method has these desirable features: (1) it can be applied to any cluster geometry (without the use of "empty spheres" or shape approximations to the density or potential); (2) it can be made arbitrarily accurate by increasing the precision of the initial pairwise fit; (3) the forces on the nucleii are available. Tests for typical molecules such as $N_2$, $CO_2$, $H_2O$, $H_2S$, and $H_2Se$ yield results in very good agreement with experiment (except for the typical overbinding due to the LDA) as well as previous state-of-the-art calculations where available.

In the present case, the muffin-tin radii were chosen 2.20 and 1.25 bohrs for Ti and C, respectively. LMTO's of kinetic energies $-0.4$, $-1.0$, and $-2.0$ Ry were used with angular momentum cutoffs of $l_{max} = 2$, 2, 1 on Ti and 2, 1, 1 on C, making a basis of 380 functions in total. The charge-density basis consisted of Hankel functions with kinetic energies $-1$, $-3$, $-9$, and $-12$ Ry with angular momentum cutoffs of $l_{max} = 3$, 6, 3, 1 on Ti and 3, 4, 3, 1 on C. Inside the spheres, the density and potential were expanded in spherical harmonics up to angular momentum $l_{max} = 3$. To speed up convergence, occupation numbers for the eigenstates were calculated using a Gaussian broadening of 0.02 Ry. With this broadening, we do not find any Jahn-Teller distortion [10]. It was found necessary to treat the high-lying Ti $3s$ and $3p$ levels with the same accuracy as the valence states by means of a "two-panel" technique.

The proposed dodecahedral structure can be viewed as a cube of Ti atoms, with one $C_2$ dimer associated with each face. Symmetry operations are mirrors on the $x$-$y$, $y$-$z$, and $z$-$x$ planes as well as the threefold rotations around the cube diagonals, generating a symmetry group of 24 elements. To calculate the equilibrium structure, the atoms were placed on the corners of an ideal dodecahedron with small random displacements to break the symmetry. While iterating to self-consistency, the atoms were moved to follow the forces until these were smaller than 0.01 Ry/bohr. In the relaxed structure, the symmetry is recovered and the C-C bond length has contracted to 2.63 bohrs while the Ti-C bond has expanded to 3.76 bohrs. The C and Ti atoms have almost the same distance from the cluster center, namely, 4.92 and 4.95 bohrs, respectively. We do not find the cubic geometry suggested in Ref. [11] on the basis of valence-bond arguments. The charge density for the valence states is displayed in Fig. 2. The calculated binding energy is
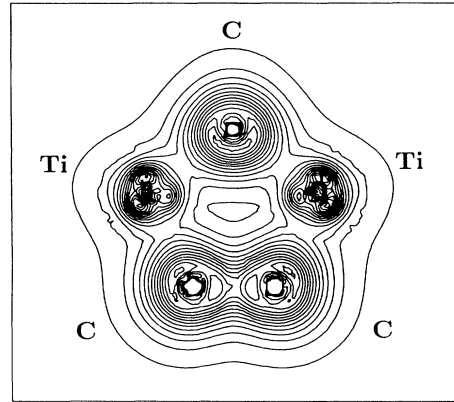
FIG. 2. Calculated valence charge density in a pentagonal face. The lowest contour and the contour spacing are 0.01 and 0.02 electron/bohr$^3$, respectively. Small discontinuities are due to the muffin-tin spheres.

6.61 eV per atom, taking into account spin-polarization energies of 0.71 and 1.20 eV, respectively, for the free Ti and C atoms. For comparison, the binding energy per atom for crystalline TiC in the NaCl structure is only slightly larger at 7.16 eV (calculated using the technique of Ref. [7]), despite the twice as large coordination number. In summary, our calculation finds the distorted dodecahedral geometry stable and strongly bound for $Ti_8C_{12}$.

When Guo et al. proposed the dodecahedral structure for $Ti_8C_{12}$, they made the reasonable suggestion that the bonding mechanism is similar to that of graphite and $C_{60}$. As first ingredient they postulated a network of Ti-C and C-C $\sigma$ bonds, involving $d$-$sp$ hybrids on the Ti atoms. Second, "$\pi$-bonding" states made from metal $d_\pi$ and carbon $p_\pi$ orbitals were assumed to take up the remaining electrons. The transition metal is assigned a relevant role in stabilizing the molecule by reducing the strain, due to the strong curvature, which would make a hypothetical $C_{20}$ molecule unstable. This model would place sixty valence electrons into the $\sigma$ bonding and twenty electrons into $\pi$ bonding states.

Our calculations support a quite different view of the electronic structure. We find that a more appropriate description is that of well-defined $C_2$ dimers whose orbitals bind with the nearest-neighbor Ti $d$ orbitals. To support this view, Fig. 3 shows the density of states for $Ti_8C_{12}$. There are four well-separated "bands" below the Fermi energy $\epsilon_F$. These correlate with the energy levels of the isolated $C_2$ dimer (calculated at the same interatomic distance as in the cluster), also shown. A Mullikan projection onto the LMTO basis set was used to decompose the density of states into site and angular-momentum contributions [12]. The two lowest bands, containing six cluster states each, are mainly of C $s$ character with a small amount of $p$ character along the C-C bond mixed in. These are derived from the $C_2$ bonding and antibonding $\sigma$ states ($1\sigma_g$ and $1\sigma_u$ in Fig. 3). The third
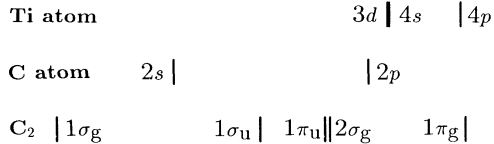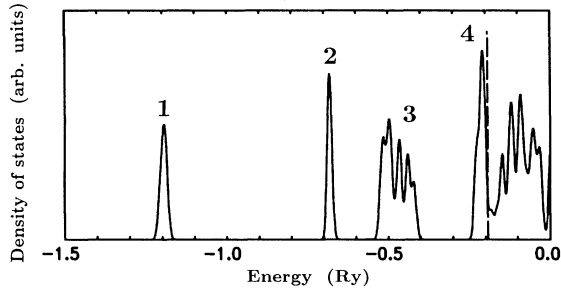
FIG. 3.   Density of states for the $Ti_8C_{12}$ molecule. Eigenvalues were broadened by Gaussians of width 0.01 Ry. The energy levels of the nonmagnetic free C and Ti atoms and of the $C_2$ dimer (with the same distance as in $Ti_8C_{12}$) are also shown.

band (eighteen states) is in the same energy range as the $p$-like bonding states in the dimer ($1\pi_u$ and $2\sigma_g$ in Fig. 3). Finally, the band just below $\epsilon_F$ (of which ten states are occupied) can be associated with the two dimer antibonding molecular orbitals, $1\pi_g$. The number of states in each band is obtained correctly by multiplying the dimer molecular orbital degeneracies with the number of dimers in the cluster (six). This classification of the cluster eigenstates is clearly visible in the partial charge densities and wave functions (Fig. 4). It is important that, in the cluster, antibonding $C_2$ dimer states are occupied which are unoccupied in the free dimer (fourth band). This indicates a transfer of charge from the Ti to the C atoms, in agreement with the electronegativities. The four bands are of 90%, 70%, 70%, and 40% carbon character, respectively. In total, we obtain valence charges of 4.36 on the carbon and 3.46 on the titanium atoms, i.e., a charge transfer of about 0.4 electron per atom. Our calculated geometry and electronic structure agree well with those of Ref. [13].

The bonding between carbon neighbors is due to the first three bands. Bonding between Ti and C atoms has some contributions from the second and third bands but is mainly due to the fourth band. Figure 5 illustrates how Ti-C bonding states can be made incorporating the $C_2$ antibonding $\pi$ states in a geometry with fivefold rings. These states weaken the C-C bonds to some extent. The unoccupied states above the Fermi energy are of practically pure Ti character and would not contribute to the bonding of the molecule if they were occupied. The energy range of this nonbonding band overlaps slightly with the fourth band. In total, there are $6 + 6 + 18 + 12 = 42$ bonding states available in the first four bands. They are filled almost completely by the eighty valence electrons. Since the Fermi level falls between the bond-
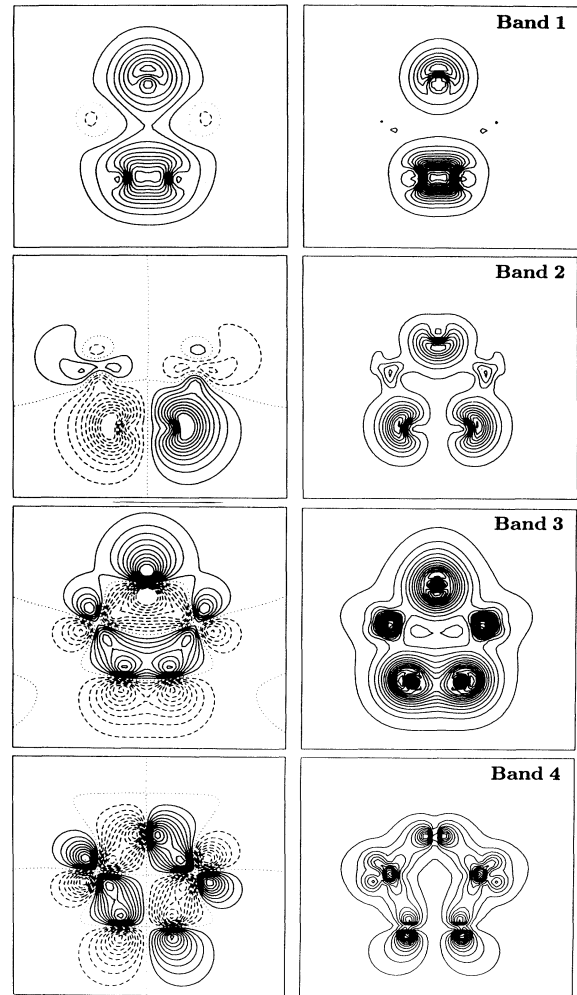


FIG. 4.   Plots in a pentagonal face of a typical wave function (left) and the summed electron density (right) for each of the four occupied bands. For the third band, the shown wave function is of $1\pi_u$ character on the $C_2$ dimer; others of $2\sigma_g$ character exist in the same band. Shown are the interstitial functions extended smoothly into the muffin-tin spheres. First contour and contour spacing are 0 and 10 for wave functions and 2.5 and 5.0 for densities in units of $10^{-3}$ bohr$^{-3}$. Negative contours are dashed; contour for zero is dotted.

ing and nonbonding states, the cluster is exceptionally strongly bound. We conclude that a similar cluster with a considerably earlier or later transition metal in place of Ti would be less stable. Interesting possibilities, however, open up if, in addition, some C atoms are replaced by neighbors in the periodic table, keeping the total number of valence electrons close to eighty. The isoelectronic metals Zr and Hf are of course obvious candidates for a stable cluster of the same type as $Ti_8C_{12}$, which indeed have been found recently [3]. For $V_8C_{12}$, the Fermi energy will be shifted upward but should still lie in the valley of the density of states.
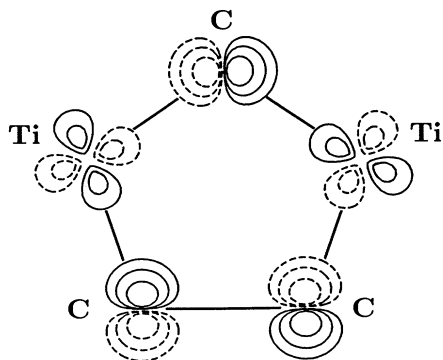
All cluster eigenstates have definite $\sigma$ or $\pi$ character

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FIG. 5. Sketch of the way in which the Ti $d$ orbitals combine with the $C_2$ dimer antibonding $p_\pi$ wave functions to make bonding cluster wave functions. The carbon atom at the top is a member of another $C_2$ dimer not in the plane of the paper.

along the C-C bond. Is it possible to classify the Ti-C bonds in the same way? The Ti $d$ orbitals which could participate hereby must be compatible with the $C_{3v}$ point symmetry at a Ti site. The arrangement of the three C neighbors is essentially a tetrahedral coordination with a missing fourth corner atom. For this symmetry it is possible to define combinations of the $d$ orbitals which are directed along the nearest-neighbor bonds. However, inspection of the forty occupied eigenstates did not yield a generally valid picture of well-defined Ti-C $\sigma$ bonding. To understand this, it is important to realize that the $C_2$ dimer forms a very strong unit in the cluster. The $C_2$ molecular orbitals, which force their shape onto the cluster wave functions, are at unusual angles relative to the Ti-C bond. An essential ingredient to the binding is the flexibility of the $d$ orbitals which makes it possible to "hook together" these functions into bonding cluster states. Of the total valence charge on the Ti atoms, only 4.5% and 3.9% is associated with the $s$ and $p$ orbitals, respectively. Thus, it is essentially only the Ti $d$ orbitals which participate in the bonding with carbon.

Nevertheless, it might be tempting to try to reinterpret our picture of the bonding as a graphitelike mechanism. This could be fueled by the fact that the number of states in the three lower bands (thirty) equals the number of possible bonding combinations of the $sp^2$-like orbitals from twenty atoms. However, this approach does not seem useful. Bonding in a graphite layer is understood to be due to two main contributions: (1) $\sigma$ bonding of localized and strongly directed $sp^2$ orbitals which point to the three neighbors; (2) additional $\pi$ bonding due to the $p_z$ orbitals perpendicular to the plane. Neither of these two mechanisms can be identified in our calculated results. We conclude that the bond of a Ti atom to its three carbon neighbors is clearly distinct from the bonding in graphite. This is confirmed by the existence of multicage structures such as $Zr_{14}C_{21}$ [14] for which no fullerene analogies exist. These structures are possible because the flexibility of the metal $d$ orbitals is sufficient to hook together four dimers instead of three. The fact

that $Ti_8C_{12}$ can bond to eight ammonia molecules was explained in a similar way [3].

In summary, our $ab$ $initio$ DFT-LDA calculation for the $Ti_8C_{12}$ molecule in the dodecahedral structure obtains a stable and strongly bound geometry. The dodecahedron is distorted somewhat because the C-C bonds are shorter compared to the Ti-C interatomic distance. The electronic structure can be understood as well-defined $C_2$ dimers whose molecular orbitals combine with the Ti $d$ functions to make bonding cluster wave functions. The Ti-C bonding is largely due to those cluster wave functions which are derived from the dimer antibonding $p_\pi$ combinations and which are unoccupied in the free $C_2$ dimer. The Fermi energy lies between the bonding states and nonbonding Ti states, explaining the stability of the cluster. Overall, we find no significant similarity to the bonding mechanism which stabilizes graphite and the $C_{60}$ molecule.

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