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Density Functional Study on the Structures and Energies of the Ti_2C_3 Cluster

Raman Sumathi* and Marc Hendrickx

Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

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The structures and energies of the binary dititanium tricarbide Ti_2C_3 in the lowest singlet, triplet, and quintet states have been investigated by density functional theory using the hybrid B3LYP functionals. Geometries and frequencies for a number of isomeric structures are presented at the B3LYP level. A pentagonal structure with a C_2 unit at the base and a carbon at the apex, **Xs**, is found to be the global Ti_2C_3 minimum. Cyclic structures **V**−**VIII** derived from the 2-fold addition of titanium to the most stable "fan" and "kite" isomers of TiC_3 are characterized as higher energy local minima. Linear structures **I**−**IV** with all probable relative positioning of the two titanium atoms have been identified as higher order saddle points with respect to the degenerate bending vibration, except for the cumulene-like valence structure **I**. Cyclic structures are energetically favored over the linear structures. A comparison with the penta-atomic group IVA silicon−carbon clusters is given, where appropriate.

Introduction

Considerable interest has been aroused lately in regard to the structures and properties of transition metal−carbon clusters. The reason for this interest ranges from the wish to gain an understanding of the chemistry of met-cars to the potential for their industrial applications. Stable metal-carbon clusters, the met-cars, having a stoichiometry $M_8C_{12}^+$ (M = Ti,V, Zr, Hf, Nb) were produced by Castleman et al.[1−3] at the beginning of this decade in molecular beams by reacting transition metal vapors with a variety of hydrocarbons. They proposed a structure for these M_8C_{12} clusters consisting of a pentagonal dodecahedron with a T_h symmetry. This is in contrast to the highly stable bulk titanium carbide cluster which crystallizes in an MX phase with a face-centered NaCl structure and is marked by strong covalent (partially ionic) bonds between the metal and the carbon atoms.[4] Further, the MX phases show marked deviations from stoichiometry. Theoretical calculations on met-cars,[5−8] however, indicate that other alternating structures (T_d or D_{2d} symmetry) slightly distorted from the T_h cage are more likely, and one such structure, T_d, has also been supported by photoelectron spectroscopy experiments.[9] Unfortunately, the theoretical calculations on these large systems are extremely difficult to perform, and hence their validity is uncertain. To understand the building-up mechanisms and the nature of chemical bonding in larger clusters, it seems inevitable to take a closer look at smaller clusters. Hence, our interest in met-cars is to identify the building blocks and to investigate the clustering phenomenon. In this regard, we wish to characterize the simpler Ti−C compounds, the potential candidates for the intermediates, and the growth species at a reliable and computationally less demanding level of theory, viz., the hybrid density functional methods. Little information seems to be available on smaller titanium−carbon (TiC_x) clusters.[10] The diatomic TiC molecule has been investigated at the complete active space self-consistent field[11,12] (CASSCF), multireference configuration interaction[11,12] (MRCI), and density functional theory[12] (DFT) levels. All calculations confirm that the ground state of TiC is the $^3\Sigma^+$ state with the equilibrium Ti−C distance varying from 1.66 to 1.76 Å with different levels of calculation. Our studies on TiC_x[13] ($x = 2-4$) at CASSCF, MRCI, and DFT levels reveal their ground-state geometry to be a ring-type structure with the coordination of titanium to all the carbons of the cluster. The C_x moiety bends slightly away from its most favorable linear configuration and leads to stable strained rings via Ti−C σ bonds. However, these clusters represent systems containing a higher proportion of carbon to the metal as compared to met-cars. Hence, the goal of the present study is to concentrate on a titanium−carbon cluster (Ti_2C_3) containing the same proportion of metal to carbon (1:1.5) as in met-cars. The present paper will therefore deal with the lowest energy structures of the various Ti_2C_3 isomers, and where appropriate, comparisons will be given with the analogous well-studied group IVA clusters (C_5, Si_5, Si_2C_3, C_2Si_3) which possess the same number of valence electrons as Ti_2C_3. Such a comparison is worthwhile to identify the impact of the fundamental differences between s^2p^2 and s^2d^2 configurations. The penta-atomic clusters C_5 and SiC_4 have been observed experimentally in the infrared range[14−17] and have been found to have a linear ground state with vibrational frequencies in good agreement with ab initio calculations.[18−20] In contrast to this linear geometry, Si_5 is predicted[21,22] to have a bipyramidal ground state, the difference being due to the tendency of carbon to form double bonds and silicon to form multidirectional single bonds. The penta-atomic mixed carbon−silicon cluster Si_2C_3 has been found both experimentally[23] and theoretically[24] to have linear ground states. The only work, to our knowledge, on Ti_2C_3 corresponds to the density functional study of Reddy and Khanna[25] using the local density approximations (LDA). They employed pseudopotentials to replace the deep cores, and their basis sets consist of 5s, 2p, and 4d Gaussians for Ti and 5s and 4p Gaussians for C. Indeed, in this study, Reddy and Khanna optimized a nonplanar structure with a C_2 base and a Ti_2 perpendicular to C−C at a height h and an apex carbon atom at a height l. They also optimized another pentagonal structure with Ti_2 being in the same plane as the remaining carbons, and they found the nonplanar structure to be the most favorable geometry. However, relevant to this study, no other structures were reported by the authors. Furthermore, it is worthwhile to mention that the met-car

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formation occurs at plasma temperature, and consequently it could involve higher energy isomers of Ti_2C_3 as intermediates in cluster growth besides the thermodynamically most stable global minimum. As a first step toward understanding, it is therefore essential to identify and characterize the different isomers of Ti_2C_3. Hence, the objective of the present study is to provide a comprehensive and detailed survey of the potential energy hypersurface of the binary Ti_2C_3 cluster.

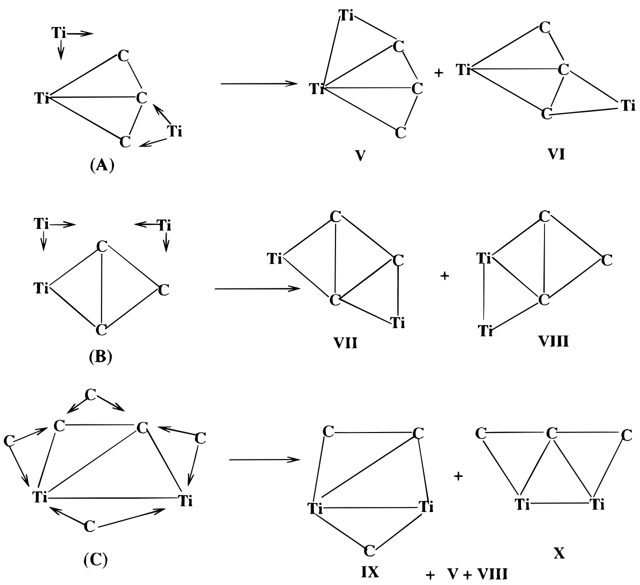
Computational Details

The DFT method was employed as a starting point for determining the various stationary points on the multidimensional Ti_2C_3 potential energy surface. Various initial structures were chosen, and a complete geometry optimization within a given symmetry group was then carried out until the structure corresponding to a stationary point was found. All such stationary points were further tested with respect to their character by a vibrational analysis checking for possible imaginary frequencies. Altogether a total of 14 stationary points have been studied.

The titanium basis set (14s,11p,6d,3f/8s,6p,4d,1f) was formed from Wachter's[26] (14s,9p,5d) basis set with the addition of Hay's[27] diffuse 3d function. The f Slater-type function (STF) exponent was taken from Bauschlicher et al.[28] and the Gaussian-type function (GTF) exponents were derived by using Stewart's contraction fits.[29] For carbon, the standard DZP (9s,5p,1d/4s, 2p,1d) basis set was used. The exchange functional in the hybrid B3LYP method[30] comprises three terms, including the Hartree−Fock exchange functional. The correlation functional is that of Lee, Yang, and Parr.[31] MULLIKEN[32] has been employed for B3LYP optimizations.

Results and Discussion

SCHEME 1



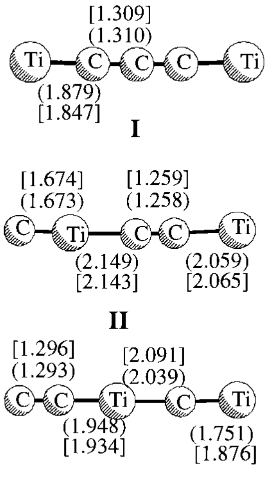


Figure 1. Optimized geometries for the triplet and quintet isomers of the linear isomers of Ti_2C_3 at the B3LYP level of theory.

Geometry optimizations have been performed for the various electronic states at the B3LYP level, starting from different nuclear arrangements that included linear, viz., with two titanium atoms in the terminal 1,5 positions (**I**), at the 1,4 positions (**II**), at the 1,3 positions (**III**), and at the 1,2 positions (**IV**); planar (**V**−**XIII**); and nonplanar ring structures (**XIV**−**XV**). Furthermore, being isovalent with TiC_4, which is found to have a ring structure ("fan"), and containing a C_4 submolecule with double bonds, the ground state could likely be a strained ring. Also, Ti_2C_3 could be visualized as the addition product of Ti to TiC_3, which is predicted[10,13] to have a planar cyclic four-membered ring structure with either a transannular Ti−C (A) or C−C bond (B) (see Scheme 1) as the ground-state geometry. The 2-fold addition of Ti to A and B leads to four possible cyclic isomers (**V**−**VIII**). Besides, Ti_2C_3 could also result from the addition of atomic carbon to Ti_2C_2, which has been found[33] to have a rhombohedral geometry (C) at the same level of theoretical characterization. The rhombohedral structure has four distinct bonds (Scheme 1) for a probable 2-fold C addition. The resulting four probable structures have been considered for geometry optimization. As is obvious from Scheme 1, out of the four possible products, two (**V** and **VIII**) have already been derived from TiC_3. The cyclic structure, **X**, could also be identified as the 2-fold addition product of two carbons to the two Ti−C bonds of Ti_2C. In this isomer, the C_3 unit is nearly linear as in an isolated C_3 cluster and possesses C−C multiple bonds which could give rise to its stability. Besides these 2-fold addition products, we have also investigated the structures of 1-fold addition of C to the rhombic Ti_2C_2 (**XI** and **XII**) and TiC_3 (**XIII**) minima. In addition to these planar cyclic isomers, two nonplanar bipyramidal isomers, **XIV** and **XV**, akin to those predicted[21,22] for the ground state of Si_5, have also been considered for geometry optimizations.

The equilibrium geometries obtained for the Ti_2C_3 isomers are given in Figures 1−4. Bond lengths are given in angstroms and bond angles in degrees. The numbers inside the parentheses and brackets correspond, respectively, to the triplet- and quintet-state geometries. Most of these isomers have geometries which allow for multiple carbon−carbon bonding, and we expect them to be energetically favored due to the relative strength of C−C bonds as compared to that of the Ti−C and Ti−Ti bonds. Table 1 gives the harmonic vibrational frequencies and intensities for the isomers of Ti_2C_3 corresponding to a local minimum. Figure 5 displays the atomic charges derived from the Mulliken population analysis for the various isomers. The relative energy of all the structures in various electronic states of Ti_2C_3 is shown in Figure 6.

Linear Structures. The lowest energy linear isomer of Ti_2C_3 corresponds to the nuclear arrangement containing two terminal titanium atoms. All linear isomers were obtained within the C_s symmetry by constraining the respective angles to be equal to 179°. The quintet electronic configuration **Iq** is favored over the triplet and singlets via Hund's rules, and it displays strong C−C and Ti−C bonding as expected for a cumulene-like

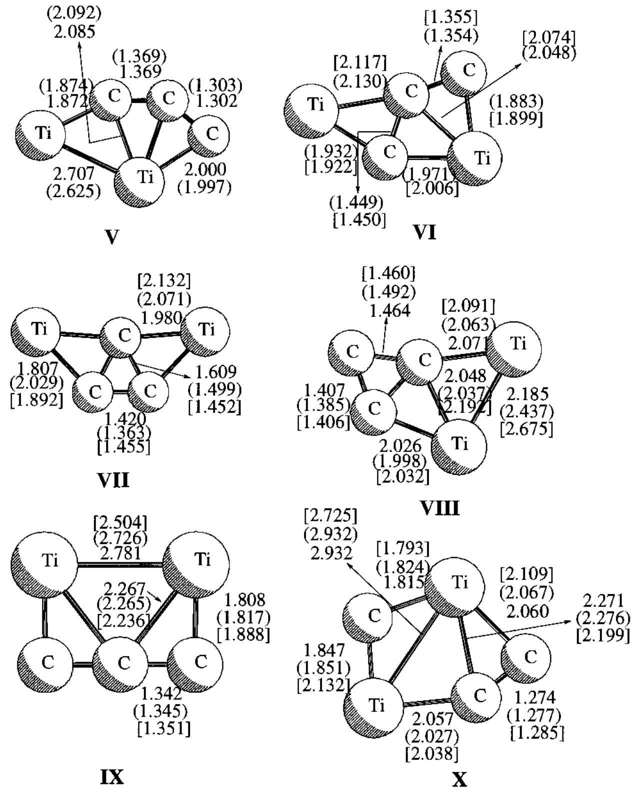


Figure 2. Optimized geometries for the singlet, triplet, and quintet isomers of the ring structures of Ti_2C_3 at the B3LYP level of theory.

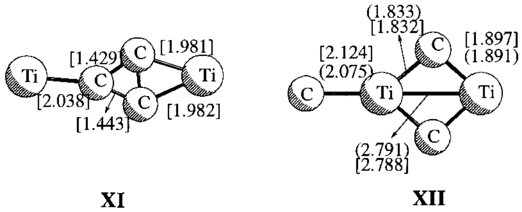


Figure 3. Optimized geometries for the triplet and quintet isomers of the ring structures with an exocylic bond of Ti_2C_3 at the B3LYP level of theory.

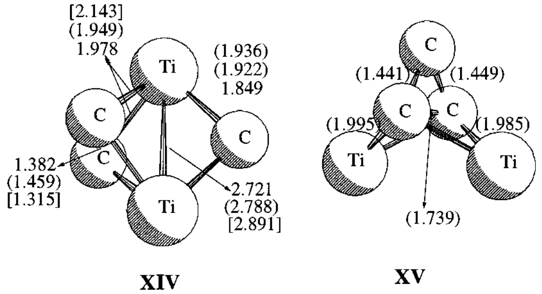


Figure 4. Optimized geometries for the singlet, triplet, and quintet isomers of the nonplanar isomers of Ti_2C_3 at the B3LYP level of theory.

TABLE 1: Unscaled B3LYP Harmonic Vibrational Frequencies of the Various Minima on the Singlet, Triplet, and Quintet Potential Energy Surfaces of the Ti_2C_3 Molecule

species	frequencies in cm^{-1}
1q	92.6, 148.6, 291.0, 305.6, 502.0, 507.9, 698.3, 1409.1, 1925.2
It	96.8, 155.5, 228.3, 275.3, 442.1, 479.9, 517.2, 1357.9, 1598.1
Vt	181.6, 209.5, 398.3, 485.8, 506.2, 629.0, 697.7, 1277.4, 1702.3
VIq	70.0, 159.4, 308.5, 518.5, 618.5, 636.2, 822.9, 1058.9, 1536.2
VIt	152.0, 287.5, 302.8, 503.6, 622.9, 652.9, 747.9, 995.7, 1449.6
VIIq	183.1, 246.3, 348.3, 364.9, 418.3, 620.3, 876.5, 1002.3, 1368.9
VIIt	218.3, 225.8, 227.6, 404.4, 425.7, 658.5, 770.4, 827.8, 1305.6
VIIs	200.2, 269.2, 330.1, 402.0, 433.7, 561.9, 768.6, 849.6, 1174.6
VIIIq	206.6, 290.5, 303.5, 310.0, 313.7, 521.5, 882.7, 1088.0, 1416.3
VIIIt	220.6, 244.5, 304.4, 314.9, 421.2, 511.2, 744.1, 941.8, 1229.6
Xt	147.4, 247.2, 267.6, 372.9, 463.4, 527.7, 715.8, 873.4, 1805.8
Xq	142.1, 212.4, 243.4, 363.1, 472.6, 481.2, 531.8, 823.3, 1749.2
XIVq	251.7, 296.0, 355.9, 368.6, 402.0, 453.2, 559.2, 664.4, 1558.6
XIVt	296.9, 337.3, 419.9, 430.5, 529.4, 594.7, 751.8, 754.4, 1080.4

valence structure in which the titaniums participate in multiple bonding. The C−C bond length (1.295 Å) is intermediate between those of a normal C−C double bond (1.35 Å in ethylene) and a normal triple bond (1.21 Å in acetylene). The C−C bond length is found to be slightly larger than the ones found in C_5 (1.271 and 1.275 Å) and falls in the range of C−C bond lengths as found[23] for SiC_4 (1.261, 1.298, and 1.259 Å). In contrast to C_5 and SiC_4 whose most stable ground-state structure corresponds to this linear isomer, in Ti_2C_3 the cyclic isomer **X** is the most favored geometry. The isomer **Iq** lies 30.3 kcal/mol above the cyclic structure **X** and is a stable minimum in its quintet and triplet B3LYP potential energy surfaces. The spin densities are located on the terminal titaniums. The linear isomer with an internal Ti atom (1,4), **II**, lies well above **Iq** and the most stable isomer, **X**, due to increased Ti−C π bonding at the expense of C−C π bonds. Curiously, **IIt** shows significant differences in the three Ti−C bond distances, one being significantly longer (2.146 Å) and the other significantly shorter (1.673 Å) than normal double-bond lengths. Isomer **IIt** could be visualized as the 1-fold addition of Ti−C to the carbon end of the linear TiC_2. As shown earlier by us,[13] linear TiC_2 corresponds to a transition state on the TiC_2 potential energy surface. The harmonic vibrational analysis of **IIt** and **IIq** reveals them to be a second-order saddle point with respect to the degenerate bending vibration.

The next linear isomer with titanium atoms in the 1,3 position, **III**, is preferred energetically in its triplet state. As can be seen from Figure 1, the structure involves a strong C−C (1.293 Å) bond and Ti−C (1.751, 2.039, and 1.948 Å) bonds. The calculated Mulliken bond orders for the terminal Ti−C and C−C bonds are 2.30 and 2.60, respectively. The Ti−C bonds are highly ionic due to the charge transfer from the metal to the carbon. As can be seen from Figure 5, the charge separation is greater whenever a titanium atom is flanked by two carbons. A similar trend has already been observed by us[13] in the linear structures of TiC_2, TiC_3, and TiC_4. However, this linear isomer also corresponds to a second-order saddle point.

The other conceivable linear structures are those with titaniums in the 1,2 (**IV**), 2,3, and 2,4 positions. We have not attempted to optimize the latter two structures. Our experience in Ti_2C, TiC_2, and Ti_2C_2 suggests that the linear structures with alternating titanium and carbon atoms would be unstable. We had problems of SCF convergence for the 1,2 isomer, and hence we are unsuccessful in optimizing this isomer in any of the electronic states.

Ring Structures Formed from the Rhombic TiC_3 Cluster (V−VIII). In searching for other energetically favored isomers of Ti_2C_3, one should expect that the formation of strong carbon−carbon bonds dominates the formation of weaker Ti−C and Ti−Ti bonds. Isomers **V** and **VI** are based on the addition of a titanium atom to the expected ground-state structure of TiC_3 (fan). Of these two isomers, isomer **V** is more stable compared with **VI** due to the obvious reason that in the latter Ti−C bonds have been formed at the expense of a C−C π bond. The attack of a titanium atom on any one of the equivalent Ti−C bonds leaves the multiply bonded carbons intact and thereby contributes to its stability. The C−C bond distances in **V** (1.303 and

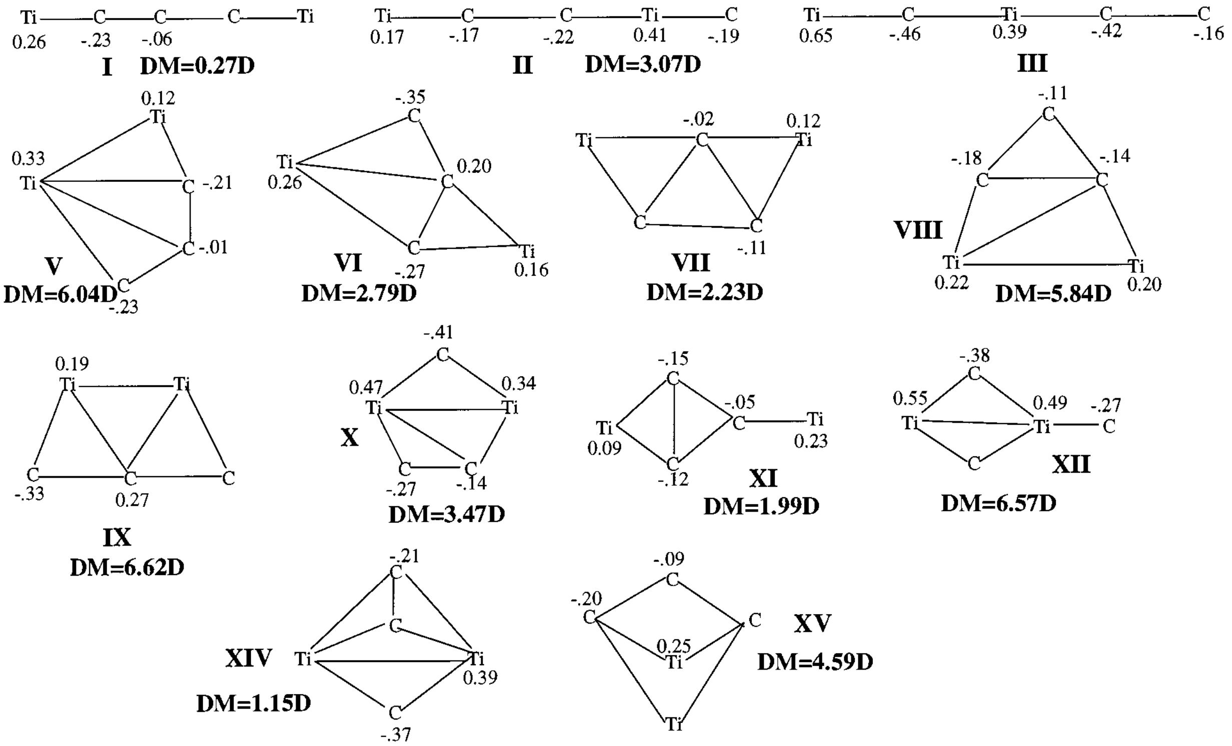


Figure 5. Atomic charges and dipole moments (in debye) for the different structures of Ti$_2$C$_3$.

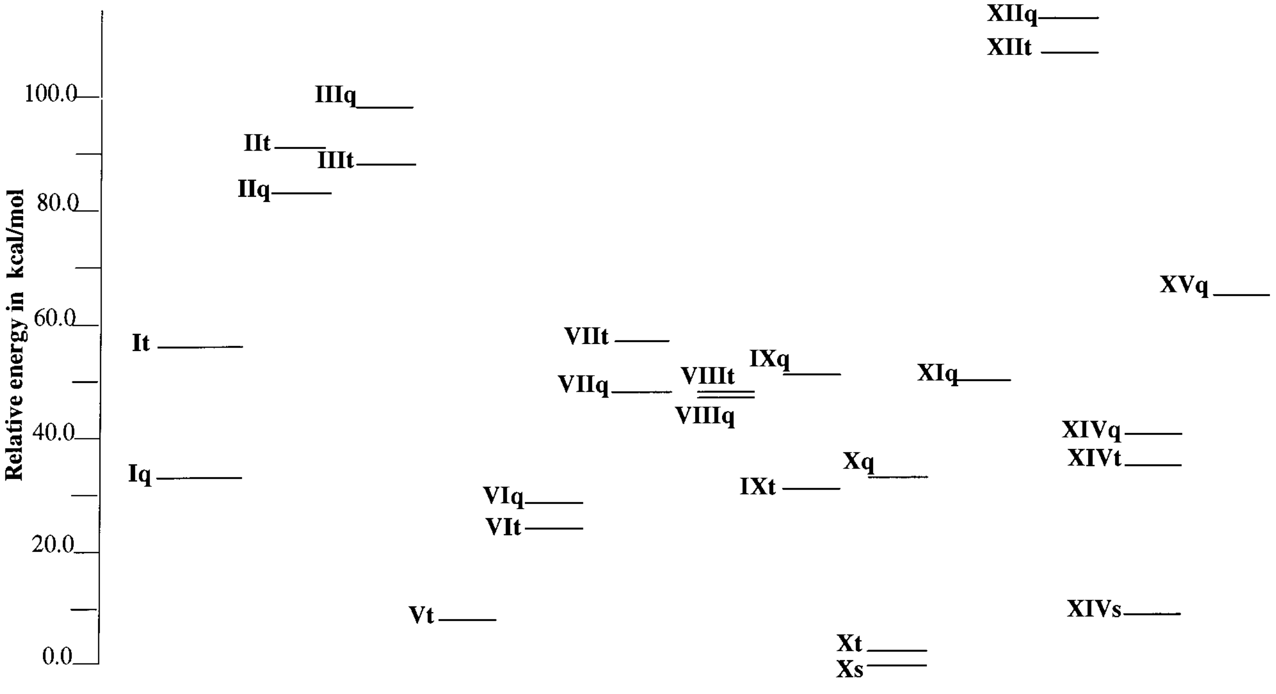


Figure 6. Plot of the relative energies (kcal/mol) of the various isomers in different electronic states of the Ti$_2$C$_3$ cluster.

1.369 Å) are indicative of a C−C double bond (Mulliken bond order of 1.79 and 1.30). The Ti−C bond distances show appreciable variations, ranging from 1.873 to 2.091 Å. The two central Ti−C bond distances are 2.071 and 2.091 Å, and their Mulliken bond orders are 0.59 and 0.74, respectively. From the Mulliken population analysis it is not clear whether this isomer possesses the transannular stabilizing bond which is typical for the rhombic TiC$_3$, SiC$_3$, Si$_2$C$_2$, and Ti$_2$C$_2$ minima. Both the singlet and triplet states are predicted to be minima, as is obvious from the vibrational frequencies in Table 1. In the alternative isomer **VI**, the C−C bond distances (1.354 and 1.450 Å) are much longer than those in **V** and hence are weakly bonded to each other (respective Mulliken bond orders are 1.41 and 0.89). Thus the coordination of titanium has occurred via the π electrons of the C−C bond, leading to a higher energy minimum.

The other two ring structures (**VII** and **VIII**) were derived from the "kite" isomer of the TiC$_3$ with a transannular C−C bond. However, in the TiC$_3$ cluster itself, for the reasons discussed above, the fan structure with a transannular Ti−C bond is more favored[13] over the kite structure with a transannular C−C bond. The C$_3$ unit is cyclic and strained and would hence disfavor its stability. Both **VII** and **VIII** are characterized as higher energy minima on the singlet, triplet, and quintet potential energy surfaces and are found to be relatively more stable in their quintet multiplicity. The Ti−C bonds in **VII** form two sets, one set being considerably stronger (1.892 Å with a Mulliken bond order of 1.50) than the other (2.132 Å with a Mulliken bond order of 0.73). Isomer **VIII** has three Ti−C bonds and a Ti−Ti bond in addition to the C_3 unit. However, the Ti−C bonds are relatively weaker compared with those in **VII**. The Ti−Ti bond order in **VIIIq** is 1.39. Inspite of the variations in the bond orders of different bonds in these two isomers, the relative stabilities of both isomers are more or less the same.

Ring Structure with a Linear C_3 Unit (IX). The isolated C_3 cluster is known to be a linear cumulene system. Twofold addition of two titanium atoms to the two C−C bonds of the C_3 unit leads to the isomer **IX**. The C−C bond distance in **IX** is 1.345 Å and is indicative of a multiple bond (the bond order is 1.42). The two titanium atoms are bonded to the terminal carbons of the C_3 unit with an optimized bond distance of 1.817 Å and to the central carbon atom with a bond distance of 2.265 Å. Under this nuclear arrangement, the two metal atoms are just 2.725 Å away from each other and hence they give rise to a strong Ti−Ti bond with a bond order of 1.638. This isomer is different from the linear isomer with two terminal titaniums viz., **I**, only with respect to the Ti−C−C bond angle. In the former, it equals 180° while in the latter it is close to 90°. The vibrational analysis of this isomer reveals it as a saddle point with respect to the Ti−C−C−Ti torsional motion.

Pentagonal Face of the Dodecahedral Structure (X). A structure similar to isomer **X** was considered earlier by Reddy and Khanna[24] in their LDA calculations as a likely structure of Ti_2C_3. However, they found a nonplanar structure energetically more favored over the planar pentagonal structure. Besides, the authors have not reported the optimized geometry of this planar structure or its relative energy. The B3LYP optimized geometry is shown in Figure 2 and has been characterized as a stable minimum on all three electronic surfaces. It is obvious from Figure 6 that the most stable structure of Ti_2C_3 corresponds to this isomer. The C−C bond located at the base of the pentagon is found to have a bond length of 1.276 Å. This value is in excellent agreement with the comparable C−C bond distance in linear Si−C−C−Si (1.28 Å for both $^1\Sigma_g^+$ and $^3\Sigma_g^-$).[34] The theoretical value for C_2 in its ground state is a bit shorter; Bruna et al.[35] obtained a value of 1.245 Å with large CI calculations. This clearly reveals the existence of multiply bonded carbons. The distance between the two titanium atoms (2.932 Å) is slightly long for a single bond, and the calculated Mulliken bond order is 0.68. The apex C−Ti bonds are relatively stronger than the base Ti−C bonds. The $\angle$Ti−C$^{\text{apex}}$−Ti with a value of 106.4° is comparable to the value of 110.0° for Ti_2C. As mentioned in the Introduction, the main difference between the predicted met-car structures and the fcc cubic structure of the bulk TiC is the existence of C_2 units in the former. The met-car with its proposed dodecahedral structure is supposed to be stabilized by TiC and C_2 units, while the cubic structure only has TiC bonds with hardly any C−C bonding. The metal-to-carbon composition of Ti_2C_3 is the same as in met-cars, and in Ti_2C_3 we found structures with C_2 units to be more stable compared with structures with isolated carbon atoms. This thereby provides support for the proposed dodecahedral structure with C_2 units for M_8C_{12}. Therefore, our investigation reveals that in carbon rich plasma with a metal-to-carbon composition exceeding 1:1 (e.g., 1:1.5 in Ti_2C_3, 1:2 in TiC_2, 1:3 in TiC_3, and 1:4 in TiC_4), the most favorable structures are those stabilized by multiply bonded C_2 units. The computed Mulliken atomic charges (Figure 5) suggest that the Ti−C bonds have ionic character as a consequence of the charge transfer from titanium to the carbons. They are associated with appreciable dipole moments due to the significant charge transfer. The extent of charge separation varies with the isomer and could probably be the cause for the variations in their total energy.

Ring Structures with an Exocyclic Ti−C Bond (XI and XII). Isomers **XI** and **XII** can be viewed as the result of a 1-fold addition of a titanium or a carbon atom, respectively, to the predicted[13] stable structure of TiC_3 and Ti_2C_2. These isomers are energetically disposed far above isomer **X**, and they have been identified as first-order saddle points from the diagonalization of their Hessian matrix. Analysis of the eigenvectors corresponding to the negative eigenvalue of the force constant matrix suggests isomer **XI** to be a transition structure for the degenerate rearrangement to **VII** and of isomer **XII** to **X**. This observation in combination with our earlier observation[13] of unstable three-membered ring structures in TiC_3 system implies that the 1-fold addition of either carbon or titanium leads to thermodynamically unfavorable products. We also considered an isomer with an exocyclic C−C bond (**XIII**) for optimization. However, optimization gives rise to the most favorable isomer **X**. No attempt has been made to optimize structures with exocyclic Ti−Ti bonds due to the fact that the Ti−Ti bond is weaker and would result, if at all, in a higher energy conformer.

Nonplanar Structures (XIV and XV). Since the bipyramidal form akin to the predicted ground state of Si_5 has been found to be a local higher energy minima in both the singlet and triplet surfaces of Si_2C_3, we have investigated here two nonplanar forms of Ti_2C_3. As found in Si_2C_3, the isomer **XIV** has been identified as a higher energy minima in triplet and quintet states and a first-order saddle point in its singlet electronic state. The bicyclic C_2Ti_2 unit in **XIV** is deformed from planarity by 65° and corresponds to the tetrahedral-like minimum of the Ti_2C_2 system with a Ti−Ti distance of 2.79 Å. As can be seen from Figure 4, this isomer could be visualized as the 2-fold addition product of carbon to the Ti−Ti bond of the tetrahedral Ti_2C_2 minimum. In Ti_2C_2, the tetrahedral structure is a competitive minimum along with the rhombic structures. Isomer **XIV** possesses a C_s symmetry, and the Ti−C bonds in the σ plane are strongly bound compared with the symmetry-related Ti−C bonds. Energetically it is more stable in its singlet state. However, the optimized structure in the singlet state corresponds to a transition structure.

The optimized structure of the tricyclic [1,1,1,0] isomer **XV** has also been given in Figure 4 and can be viewed as a 2-fold addition of carbon to the C−C bond of the nonplanar Ti_2C_2 structure. The bridgehead C−C bond distance equals 1.74 Å leading to skeptical C−C bonding. The calculated Mulliken bond order for the bridgehead C−C bond is 0.39. Isomer **XV** indeed is a metal carbene since the other two C−C bond distances are indicative of σ-bonded carbons. The vibrational analysis of this structure reveals it as a saddle point with respect to the ring bending vibration of the C_2Ti_2 unit leading to isomer **XIV**.

To summarize, the procedures applied in this paper illustrate one of the basic ways to generate isomeric structures of a particular Ti_nC_m cluster, viz., to start with a known low energy structure of an $n - 1$ or $m - 1$ cluster followed by the 2-fold or 1-fold addition of a titanium or a carbon atom, respectively. Also, our investigations on Ti_2C_3 and TiC_x ($x = 2$, 3, or 4) systems containing a higher proportion of carbon to the metal (viz., 1:1.5 in Ti_2C_3, 1:2 in TiC_2, 1:3 in TiC_3, and 1:4 in TiC_4)

reveal that the isomers with multiply bonded carbons are more stable compared with multiply bonded titanium. This confirms the presence of undissociated C_2 units in met-cars, which are produced only in carbon-rich plasma. Unlike the analogous group IVA disilicon tricarbide, which was shown experimentally by Presilla-Marquez and Graham[23] to have a linear structure continuing the "C_5 -like" trend for the penta-atomic silicon−carbon cluster, Ti_2C_3 is anticipated to have a ring structure from our calculations. As is obvious from Figure 6, several isomers exist as minima within 100 kcal/mol of energy from the global minimum. In plasma temperature, the relative population of all these higher energy isomers would be appreciable and hence there exists a certain probability for them to play a role in the met-car formation.

Conclusions

The results of our calculations predict a cyclic pentagonal structure (**X**) for the ground-state molecular structure of Ti_2C_3. Various other ring structures (**V**−**VIII**) also correspond to minima, however, with higher energies. Besides these planar ring structures, calculations also suggest a nonplanar minimum (**XIV**) for Ti_2C_3. Ring structures with exocyclic double bonds (**XI** and **XII**) are identified as transition structures with respect to the degenerate rearrangement to the cyclic structures. The comparison of the preferred geometries of Ti_nC_m clusters (n = 1 or 2; m = 2, 3, or 4) with the analogous group IVA silicon−carbon clusters is as follows: SiC_2 (cyclic, C_{2v}) is similar to TiC_2; SiC_3 is rhomboidal as is TiC_3, but with a transannular C−C bond instead of an Si−C bond; and SiC_4 and Si_2C_3 are linear, contrary to TiC_4 and Ti_2C_3 which are cyclic. The Ti−C bonds are highly ionic, and the main energy difference between the various isomers comes from the delocalization of the transferred charge from Ti to the carbons. The calculated ground-state geometries and frequencies will be valuable in identifying these clusters experimentally and in turn in testing the validity of the DFT predictions. Clearly, theoretical calculations on additional Ti_nC_m clusters are needed to elucidate the intermediates involved in the cluster formation, to identify the growth species, and to investigate the clustering phenomenon.

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