

Ti₈C₁₂: a Polytopal Molecule with 36 Ti–C Bonds

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The Ti₈C₁₂ molecule, recently observed as a positive ion by Castleman *et al.*, is presented as a cluster with seven possible conformations which have been characterized as local minima by means of *ab initio* Hartree–Fock calculations.

A recent report by Dance¹ and calculations independently carried out in our group^{2†} have shown that the remarkable stability of the Ti₈C₁₂ cluster previously characterized by mass spectrometry by Castleman *et al.*³ could be explained by a cage structure allowing for 36 metal–carbon interactions.‡ The cage structure with *T_d* symmetry§ optimized by Dance using local density calculations is characterized by six *C₂* units occupying the 'butterfly' units of a Ti₈ tetracapped tetrahedron.¹ In independent work, geometry optimization processes carried out using the Hartree–Fock (HF) and the local density (LDA) approaches respectively, have led to two different structures, both distinct from Dance's *T_d* cage.^{2†} All three optimal structures have interesting similarities however. In fact, the three conformations can be viewed as strongly distorted cubes of titanium atoms with the six *C₂* units parallel

to the longest diagonal of the underlying face. All three computed cluster cages give rise to 36 metal–carbon distances within bonding range.

Considering the results of the calculations reported in ref. 2,† we conjectured that each *C₂* unit could be oriented along one or other diagonal of the underlying face of the pseudo-cubic framework, independently of other dicarbon fragments. With this assumption, the Ti₈C₁₂ cluster can be considered as a polytopal system with a maximal number of 2⁶ = 64 conformations that are likely to be local minima of the potential hypersurface. This would explain why distinct optimization processes have led up to now to three different structures. In fact, no more than seven among those 64 structures are topologically distinct (Fig. 1). Those seven structures share some common features, the most important one being the total number of 36 metal–carbon interactions. However, those structures differ one from another by three characteristics:

(i) *The symmetry group to which they belong.* This group can be either *C₃* (structure *g* in Fig. 1, and occurring 24 times), *D₂* (*f*, 12 times), *C_{2v}* (*e*, 12 times), *D_{2d}* (*d*, 6 times), *D_{3d}* (*c*, 4 times), *D_{3d}* (*b*, 4 times) and *T_d* (*a*, 2 times).

(ii) *The deformation of the pseudo-cubic framework.* In each conformation, the metal framework deforms according to the constraints of the symmetry group and to the orientation of the capping *C₂* units in order to reduce the difference in bond lengths between short, end-on Ti–C bonds on the one hand, and long, side-on Ti–C bonds on the other hand. As a result, each *C₂* unit is oriented along the longest diagonal of the underlying Ti₄ quadrangle. This leads to the butterfly deformation reported by Dance for the *T_d* conformation, and also present in the conformations with *D_{2d}* and *C_{2v}* symmetries. In conformations (*b*) and (*c*) belonging to the *D_{3d}* point group, those deformation trends lead either to an elongation (form *b*) or to a flattening (form *c*) of the framework along the *C₃* axis (Fig. 2).

(iii) *The distribution of the Ti–C bonds among the eight apices of the pseudocube.* If every carbon atom is involved in three Ti–C bonds, irrespective of structure, a specific titanium

† Starting from the Jahn–Teller distorted geometry with *D_{2h}* symmetry optimized for the complex with 24 Ti–C bonds in the 20 π electron configuration,⁷ we carried out a geometry optimization without symmetry constraints using the local density approach. The calculations were carried out by means of the Unichem-DGauss program.¹³ This optimization process eventually converged towards a structure with 36 Ti–C bonds, very close to the *C_{2v}* symmetry and corresponding to conformation (*e*) of Figs 1 and 2. The energy was decreased by as much as 0.6086 Hartree with respect to the starting conformation. In parallel to that work, a geometry optimization was carried out at the Hartree–Fock level subject to the symmetry constraints of the *S₆* point group, starting from a structure with *T_h* symmetry. That calculation converged toward structure (*b*) (*D_{3d}* symmetry) with an energy improvement of 0.6053 Hartree. Other theoretical investigations on metallocarbohedrenes (metcars) are reported in refs. 4–12.

‡ It is interesting to note that, at variance with the *T_h* structure of a pentagonal dodecahedron initially proposed for Ti₈C₁₂, the structures with 36 Ti–C bonds are stable with respect to titanium carbide and residual graphite.⁵

§ In ref. 1, the structure with lowest energy was erroneously assigned the *T_h* symmetry.

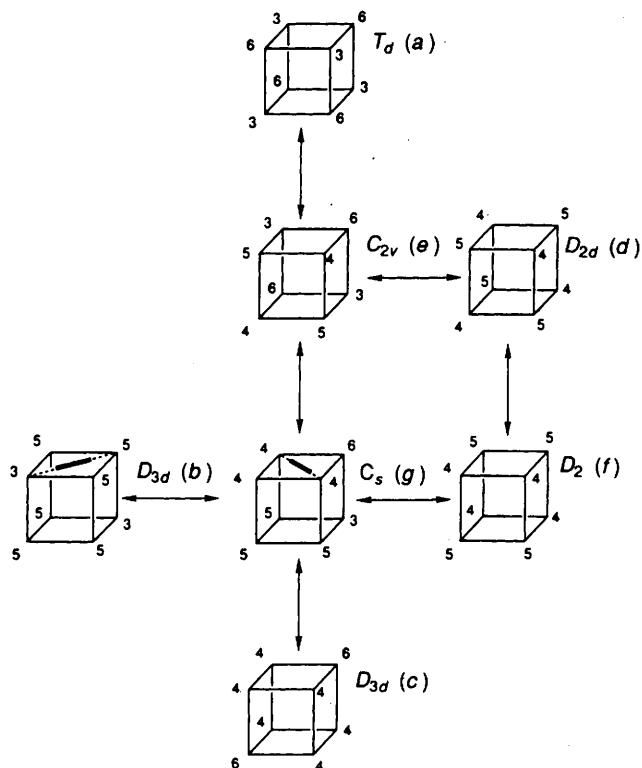


Fig. 1 Schematic representation of the seven distinct topological structures that are shown to be local minima on the potential hypersurface of Ti_8C_{12} . The cubes symbolize the metal framework and the numbers associated with each apex stand for the number of carbon atoms at bonding distance. The transition from one structure to another is represented by double arrows assuming the topological change to result from the 90° rotation of only one C_2 fragment. The rotating dicarbon unit is explicitly represented to illustrate the transition between the structures *g* (C_s) and *b* (D_{3d}).

atom takes part into 3, 4, 5 or 6 metal-carbon bonds depending on the coordination modes, end-on or side-on, of the three adjacent dicarbon units. The distribution of the Ti-C bonds among the titanium atoms is characteristic of each conformation and can be used as an unambiguous representation (Fig. 1).

The geometries corresponding to the seven structures outlined in Fig. 1 have been determined by means of gradient optimization at the one-configuration Hartree-Fock level, using the TURBOMOLE program.¹⁴ The sizes of the basis sets used for the calculations are (13s, 8p, 5d) for Ti and (9s, 5p) for C, respectively contracted into [5,3,3] and [3,2]. More details about the basis sets are given in ref. 7. The optimization processes have been subjected to the constraints of the symmetry point group assigned to each structure (Fig. 1). It has been verified for each configuration that all eigenvalues of the final Hessian matrix are positive. Closed shell electronic structures were assigned to all conformations, except to conformation (*a*) with T_d symmetry for which a one-determinant low-spin configuration leads to an unreasonable coupling of the metal valence electrons. The optimal structures and their relative energies at the one-configuration HF level are displayed in Fig. 2.

All structures with 36 Ti-C bonds are more stable by 250 to 450 kcal mol⁻¹ (1 cal = 4.184 J) than the low-spin configuration with 20 π electrons previously optimized for the structure of a pentagonal dodecahedron.⁷ The recent characterization by Hay of a set of 12 π electron configurations for the T_h structure with 24 Ti-C bonds¹² provides renewed interest for an energy comparison between the two types of cage structures. The most stable configuration proposed by Hay is a high-spin state with eight singly occupied metal orbitals

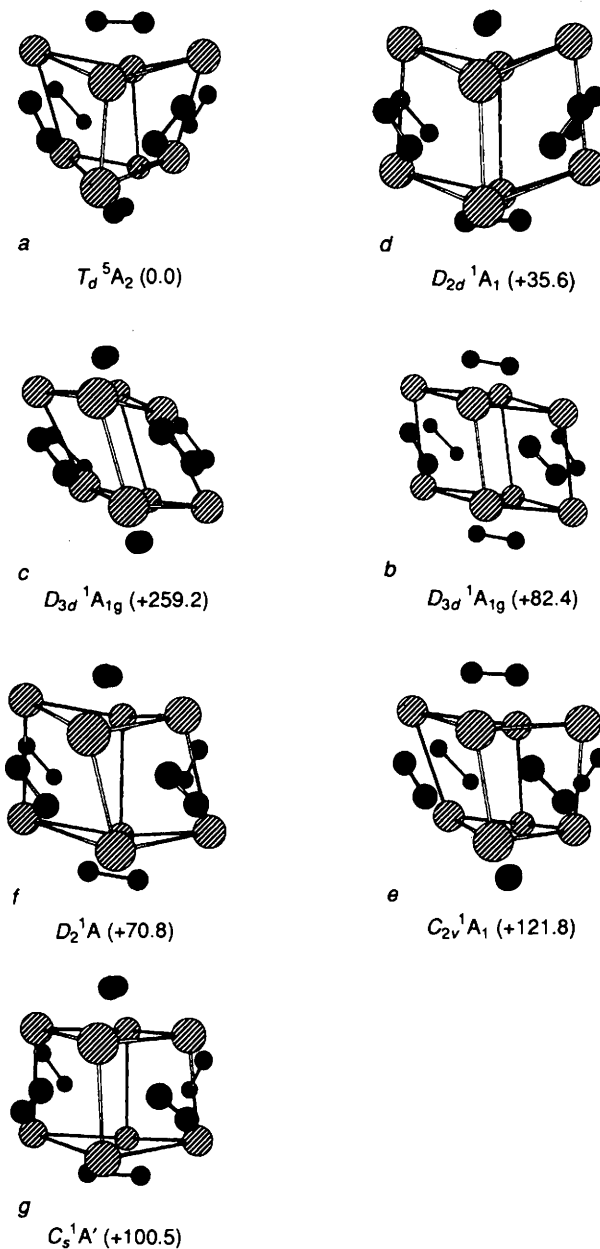


Fig. 2 Geometrical representation of the seven topological structures of Ti_8C_{12} as optimized by means of one-configuration Hartree-Fock calculations. The relative stability (kcal mol⁻¹) of those conformations is indicated, as obtained at this level of calculation.

oriented along the body diagonals of the Ti_8 cube.¹² Even though this electronic state of the T_h cluster is more stable by 250 kcal mol⁻¹ than the lowest state with 20 π electrons, there is little doubt that it is destabilized with respect to all structures with 36 bonds. A reliable energy comparison is provided by Dance.¹ This LDA study concludes in favour of the T_d form with an energy gap of 350 kcal mol⁻¹ with respect to the T_h structure. In another work also based upon LDA calculations, Chen *et al.*¹¹ show that the Zr_8C_{12} cluster in T_h symmetry is unstable owing to the occurrence of twelve imaginary frequencies after diagonalization of the dynamic matrix. We suggest that the dodecahedron structure in a 12 π electronic state could correspond to the transition state connecting all seven 36-bond conformations on the potential hypersurface. Another possibility, illustrated by the double arrows of Fig. 1, implies one-to-one correspondences between the seven local minima, assuming the topological change from one form to

another to result from the 90° rotation of one C–C fragment only.

We wish to discuss now in more detail the electronic structure of the T_d form that was found to be the most stable at the one-configuration HF level, and to gain some insight into the effect of electron correlation. All closed-shell electronic states optimized in the present work are characterized by a manifold of 10 doubly occupied frontier orbitals with dominant metal character, stabilized through bonding interactions with the high-lying σ and π^* orbital combinations of the C_2 fragments with appropriate symmetry. The energy of those frontier MOs is typically between -0.2 and -0.3 Hartree. No such electronic configuration could be obtained within the constraints of the T_d point group. The one-determinant state with lowest energy for this symmetry is a quintet 5A_2 corresponding to the following distribution of the 80 valence electrons: $(4a_1)^1(4e)^4(3t_1)^6(7t_2)^3$; $E = -7228.39247$ Hartree. The four singly occupied orbitals are localized on the vertices of the innermost tetrahedron of metal atoms, which are surrounded each by six carbons in a near-planar, side-on coordination mode [Fig. 2(a)]. Those d_{z^2} like orbitals are oriented each along a C_3 axis of the tetrahedron. This electronic configuration is therefore reminiscent of the nonet state characterized by Hay for the T_h structure.¹² The singly occupied orbital with a_1 symmetry corresponds to an in-phase, fully bonding combination of the 4 d_{z^2} -like orbitals, whereas the semi-occupied orbitals with t_2 symmetry are nonbonding. The metal–metal distances in the innermost tetrahedron are short enough (3.114 Å) to give rise to a significant overlap stabilizing the $4a_1$ singly occupied MO (orbital energy, $e = -0.153$ Hartree), with respect to the t_2 set ($e = -0.057$ Hartree). A more precise evaluation of the effect of metal–metal interactions is obtained from the characterization of another quintet state with same formal distribution of the valence electrons among the irreducible representations, but localizing the singly occupied orbitals on the vertices of the outermost tetrahedron of Ti atoms. The corresponding Ti–Ti distances (4.84 Å) are out of range for metal–metal bonding and the energy of the totally symmetric SOMO ($e = -0.068$ Hartree) becomes similar to the orbital energy of the nonbonding triad ($e = -0.057$ Hartree). The energy of that configuration is -7228.22687 Hartree, destabilized by 104 kcal mol⁻¹ with respect to the former quintet. Without neglecting the influence of charge reorganization, the energy difference should be attributed, at least in part, to the effect of metal–metal interaction. Populating the $4a_1$ MO with two electrons leads to a 3T_1 configuration corresponding to the valence electron distribution $(4a_1)^2(4e)^4(3t_1)^6(7t_2)^2$ and to an energy of -7228.23825 Hartree.

The C–C distances optimized for the 5A_2 state of lowest energy (Q) and for the 3T_1 state (T) are very similar (1.343 Å for Q, and 1.335 Å for T), and so are the Ti–C distances (end-on: 1.964 Å for Q, 1.963 Å for T; side-on: 2.265 Å for Q, 2.247 Å for T). Logically, the Ti–Ti distances inside the innermost tetrahedron of metal atoms are significantly shorter for T (2.865 Å) than for Q (3.114 Å) because of the double occupancy of the totally symmetric combination of metal orbitals, $4a_1$. Those distances, especially those obtained for T, compare well with the geometry optimized by Dance.¹

As stated above, the symmetry constraints of the T_d point group prevent the characterization of a closed-shell configuration with orbital $4a_1$ being doubly occupied. Such a configuration can however be found by means of a Jahn–Teller deformation breaking the T_d symmetry into D_{2d} . The t_2 representation of the T_d group transforms into $b_2 + e$ and the electron pair occupying the $7t_2$ orbital in the 3T_1 configuration can be assigned to the b_2 representation of the D_{2d} group, then leading to the closed-shell configuration $(8a_1)^2(3a_2)^2(4b_1)^2(7b_2)^2(9e)^4$. An SCF optimization of the 1A_1 configuration under the constraints of the D_{2d} point group yielded an energy value of -7228.36480 Hartree, close to that of the quintet

state, but associated with a structure severely distorted with respect to the tetrahedral symmetry. This competition between a high-spin, highly symmetric configuration, and a low-spin, Jahn–Teller distorted one is once again reminiscent of the discussion on the dodecahedral structure,¹² even though the energy gap appears to be much smaller in the present case. It is suggested that high-spin configurations similar to the quintet state of the T_d form could also be characterized for other structures with 36 Ti–C bonds.

We now discuss the coupling of the four metal unpaired electrons in the conformation with T_d symmetry as obtained from configuration interaction. An examination of the open-shell wave functions associated with the triplet and with the quintet states shows that the frontier orbitals $4a_1$ and $7t_2$ are different phase combinations of the same d metal atomic orbitals. Such a situation is likely to yield symmetry-breaking artefacts¹⁵ reminiscent of the artificial delocalization of molecular core–hole states imposed by the symmetry constraints.¹⁶ The zeroth-order description of the ground and lowest excited states is given in such a case by multiconfiguration expansions allowing for a convenient relocation of the metal electrons.¹⁷ This was obtained in the present case by means of full CI expansions on the limited subspace composed of the four frontier orbitals ($4a_1$ and $7t_2$) ensuring an appropriate coupling of the four electrons for all possible spin multiplicities. It appears from those calculations that the state lowest in energy is not the quintet state optimized at the HF level, but a totally symmetric singlet state 1A_1 . This singlet coupling of the four unpaired electrons is expressed by means of a combination of eight configuration state functions, six of which have individual weights higher than 10%. The energy of the singlet ground state, at the geometry optimal for the 5A_2 state, is -7228.40269 Hartree. The 3T_1 state is a combination of four configurations, destabilized by ca. 2 kcal mol⁻¹ with respect to the ground state. The 5A_2 state is the unique quintet state to appear in the CI space. Its SCF energy therefore remains unaffected at $+6.5$ kcal mol⁻¹ with respect to the ground state. Similar calculations carried out at the geometry optimal for the one-configuration triplet yielded slightly higher energies with larger splitting between the states ($^1A_1 = -7228.39055$ Hartree; 3T_1 at $+4$ kcal mol⁻¹; 5A_2 at $+14$ kcal mol⁻¹).

Multireference CI expansions have then been carried out in order to correlate the 20 electrons accommodated in the manifold of frontier orbitals with major metal character. The geometry was that optimized for the quintet state and the reference space was composed of the set of configurations properly describing the coupling of the four unpaired electrons (8 reference configurations for the singlet state, 4 for the triplet, 1 for the quintet). The total energy obtained for the singlet ground state at this level of correlation is -7228.74917 Hartree (Davidson's correction not included). The total weight of the reference set is 0.90 and all other configurations have coefficients smaller than 0.05. The energy gaps with the triplet and with the quintet states become 4.2 and 10.5 kcal mol⁻¹, respectively. We expect this level of correlation to provide a balanced comparison between the energies of the different structures within the framework of the HF methodology. Preliminary calculations carried out at this level on structures (b) and (c), both with D_{3d} symmetry, indicate that those two structures can be described in terms of one dominant configuration with respective weights 0.92 and 0.88 in the CI expansion. The energies associated with the correlated wave functions are -7228.4956 Hartree for (b) and -7228.4968 Hartree for (c) (Davidson's correction not included). The energy gap with respect to the T_d structure is then ca. 160 kcal mol⁻¹ for both structures, strongly at variance with what was obtained at the Hartree–Fock level (Fig. 2).

To summarize, one-determinant Hartree–Fock calculations show that seven local minima can be characterized on the

potential hypersurface of Ti_8C_{12} , corresponding to topologically distinct conformations. All structures display 36 Ti-C bonds, but they differ each from another by the coordination spheres of the metal atoms and by the symmetry point group to which they belong. The configuration with lowest energy at the one-configuration Hartree-Fock level is the form with T_d symmetry previously characterized by Dance.¹ The ground state electronic structure of the tetrahedral conformation corresponds to the coupling into a totally symmetric singlet state of a set of four unpaired metal electrons. The metal-metal interactions play an important role in the stabilization of that cluster. The six other conformations were described in terms of one-configuration closed-shell singlet states, but there are some hints that electronic configurations involving unpaired electrons can compete with those reported in the present work. Electron correlation appears necessary to obtain a balanced and reliable estimate of the relative stabilities of the seven forms. Work in that direction is in progress, in parallel with an attempt to design the potential hypersurface of Ti_8C_{12} by means of the local density approach.

The HF calculations have been carried out in part on an IBM RS 6000 workstation purchased with funds provided by DGICYT of Spain Government (PB89-0648-C02-02), and in part on the Cray-2 computer of the Centre de Calcul Vectoriel de la Recherche (Palaiseau, France). The LDA calculations² have been carried out on a single cpu of a Cray Y-MP8E/8128 located at Cray Research, Inc, 655 Lone Oak Drive, Eagan, MN 55121. We are pleased to thank Profs. J. Almlöf, E. Pénigault and R. Wiest for fruitful discussions.

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