enzymatic hydroxylation of the aromatic ring or incorporation of the phenolic hydroxyl to the aryl precursor **4** as suitable modifications for the synthesis of pancratistatin (**1**). We will report on the progress toward this goal in due course.

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Supplementary Material Available: Experimental procedures and spectral data (^{1}H-NMR and ^{13}C-NMR) for compounds **9b**, **10b,c**, **11–13**, and **3** (4 pages). Ordering information is given on any current masthead page.

Jahn–Teller Distortion Predicted for Metallocarbohedrenes: An ab Initio SCF Geometry Optimization of the Lowest Singlet and Triplet States of Ti_8C_{12} in the T_h and D_{2h} Point Groups

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The existence of a new class of stable clusters has just been postulated from the exceptional abundance of the ionic species $M_8C_{12}^+$ (M = Ti, V) in the distribution of metal–carbon clusters obtained from reactions of the metal with hydrocarbons.[1-3] It has been proposed that the prominence of the M_8C_{12} cluster arises due to its presence as a neutral species. The unusual stability of M_8C_{12} is taken as a strong argument in favor of the cagelike structure of the pentagonal dodecahedron with T_h symmetry proposed by Guo et al.,[1-3] which is reminiscent of another cage structure with exceptional stability, the famous buckminsterfullerene, C_{60}.

We report the first quantum chemical calculations on Ti_8C_{12}. Those calculations have been carried out at the ab initio SCF level[4] using the ASTERIX program system.[7] Since no experimental structure is available yet, the geometry of the lowest closed-shell singlet state has been optimized using an analytical gradient technique.[8] In a first series of calculations, the constraints of the T_h symmetry point group have been imposed along the complete process of geometry optimization. Accounting for the 80 valence electrons, the lowest singlet state in the T_h symmetry can be labeled as

$$ {}^1A_g \qquad (4a_g)^2(1a_u)^2(3e_g)^4(1e_u)^4(3t_g)^6(6t_u)^6 \tag{1}$$

Only three geometrical parameters are independent under the constraints of the T_h group and require optimization, namely, the radius of the "metal sphere" containing all Ti atoms, the radius of the carbon sphere, and the C–C distance. The optimal values for those parameters and for the corresponding Ti–Ti and Ti–C distances are reported in Table I. The HOMO, $4a_g$, corresponds to a poorly stabilized, in-phase combination of the metal 4s orbitals, with negligible contribution (4%) from the carbons. The low-lying LUMO, $4t_g$, results from a stabilizing interaction between the carbon π^* orbitals and appropriate combinations of the d_{x^2,y^2,z^2} metal orbitals. It immediately appears from the weak HOMO–LUMO gap (0.063 hartree or 1.7 eV; Table I) that the promotion of an electron pair from $4a_g$ to the triply degenerate orbital $4t_g$ will lead to a stabilized triplet state. As a matter of fact, two low-lying triplet states have been characterized at the open-shell SCF level of calculation by populating $4t_g$ with either two or four electrons. The corresponding states are labeled as

$$ {}^3T_g \qquad (3a_g)^2(1a_u)^2(3e_g)^4(1e_u)^4(4t_g)^2(6t_u)^6 \tag{2}$$

and

$$ {}^3T_g \qquad (3a_g)^2(3e_g)^4(1e_u)^4(4t_g)^4(6t_u)^6 \tag{3}$$

and the total energies respectively associated with states 2 and 3 at their optimal geometries are lower by 0.171 and 0.233 hartree than that of state 1 (Table I).

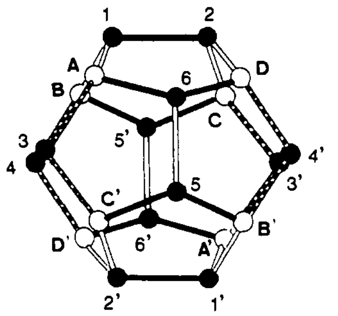

Figure 1. Computed structure of the Ti_8C_{12} cage molecule along the D_{2h} distortion path. White circles, labeled A–D, correspond to titanium atoms; black circles, labeled 1–6, to carbon atoms. Bold lines represent short bonds (carbon–carbon, 1–2 = 1.299 Å; titanium–carbon, A6 = D6 = B5′ = C5′ = 1.952 Å); thin lines represent long bonds (C–C, 5–6 = 1.478 Å; Ti–C: A1 = B1 = C2 = D2 = 2.145 Å); broken lines represent intermediate bonds: (C–C: 3–4 = 1.392 Å; Ti–C: A3 = B4 = C3′ = D4′ = 2.067 Å). The Ti–Ti distances are as follows: BC = AD = 3.033 Å; AC′ = BD′ = 3.198 Å; AB = CD = 3.275 Å (see Table I). When a T_h symmetry is assumed for the cage, all C–C bonds, all Ti–C bonds, and all Ti–Ti distances become equivalent.

In state 3, the energy gaps separating the HOMO from the partly occupied molecular orbitals (POMO), on the one hand, and the POMO from the LUMO, on the other hand, are large enough to suggest that the considered state is the lowest state of the Ti_8C_{12} cage *as far as the symmetry constraints of the T_h point group are applied to the wave function.*

As shown by Jahn and Teller,[9] degenerate electronic states such as states 2 and 3 cannot exist, except for linear molecules, since they cause structural instability. In order to explore the effect of this first-order Jahn–Teller (FOJT) distortion, the degenerate character of the wave function was removed by allowing the four electrons equally distributed in the triply degenerate POMO to be accommodated in two orbitals only, thus giving rise to a closed-shell singlet configuration with D_{2h} symmetry:[10]

$$ {}^1A_g \qquad (9a_g)^2(4b_{1g})^2(4b_{2g})^2(3b_{3g})^2(2a_u)^2(6b_{1u})^2(6b_{2u})^2(6b_{3u})^2 \tag{4}$$

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(4) The Gaussian basis set used for titanium is a (13s, 8p, 5d) set obtained by adding one p function of exponent 0.15 to the set optimized by Hyla-Kryspin et al.[5] It was contracted into [5, 3, 3]. The basis set used for carbon is a (9s, 5p) set taken from Huzinaga[6] and contracted into [3, 2]. The molecular basis set is then made of 824 Gaussian functions, and the number of contracted orbitals is 364.

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Table I. Optimal Geometry, Total Energy, and Energy of the Frontier Orbitals for States 1–3 (T_h) and for State 4 (D_{2h})

	1[a]	2[a]	3[a]	4[a]
optimal geometries (Å)				
M_0–Ti[b]	2.701	2.713	2.705	2.745
M_0–C	2.614	2.595	2.592	2.609, 2.748, 2.546
C–C	1.391	1.435	1.402	1.299, 1.392, 1.478
Ti–Ti	3.119	3.133	3.123	3.198, 3.033, 3.275
Ti–C	2.025	2.008	2.013	2.145, 2.067, 1.952
total energy[c]	−0.38279	−0.55345	−0.61641	−0.66187
nature and energy (eV) of the frontier orbitals				
HOMO	$4a_g$ −2.31	$1a_u$ −4.11	$6t_u$ −5.14	$6b_{2u}$ −4.35
POMO		$4t_g$ −1.74	$4t_g$ −3.32	
LUMO	$4t_g$ −0.60	$7t_u$ 1.36	$1a_u$ 0.49	$3a_u$ 0.79

[a] State 1, ^1A_g; state 2, ^3T_g; state 3, ^3T_g; state 4, ^1A_g. See text for a more detailed description. [b] M_0 represents the center of symmetry of the cluster. [c] Hartree; shifted by −7227 hartrees.

A preliminary calculation carried out at the geometry optimal for state 2 yielded the total energy −7227.62241 hartrees. Even though no *geometrical* deformation has been introduced yet, this trial value is already lower than the energy associated with any wave function satisfying the constraints of T_h symmetry.[11]

Finally, a gradient optimization has been carried out on the nine independent geometrical parameters that condition the structure of Ti_8C_{12} in the D_{2h} symmetry. The optimal values and the associated energy are reported in Table I. The distortion with respect to a totally symmetric cage structure is important, especially for the six C–C bonding distances that are split into two "short" bond lengths of 1.30 Å, two "intermediate" ones of 1.39 Å, and two "long" C–C bonds of 1.48 Å. Short C–C bonds are associated with long Ti–C bonds and vice versa (see Figure 1). The HOMO–LUMO gap now amounts to 0.19 hartree (5.2 eV, Table I). This is significantly smaller than the gap computed for C_{60} by Scuseria[12] with a double-ζ basis set (0.28 hartree, 7.6 eV), possibly suggesting less kinetic stability for Ti_8C_{12}. However, the LUMO of Ti_8C_{12} has a positive energy, at variance with that of the strongly electrophilic buckminsterfullerene.[13] With 66% weight on the titanium atoms, the HOMO of the distorted structure ($6b_{2u}$) takes place on the top of a set of 10 occupied orbitals with predominant metal character, spanning the energy range −4.35 to −6.9 eV. This cluster of metal frontier orbitals is separated from the highest carbon π orbital ($9a_g$, −9.2 eV) by an energy gap of 2.3 eV. The Mulliken net charge on the metal atoms is +1.1*e*, and the negative charge is almost equally distributed among the three types of carbon atoms (−0.72, −0.72, and −0.77*e*).

In conclusion, we predict the cage structure assumed for Ti_8C_{12} to be subject to FOJT distortion because of the degenerate character of the triplet ground state characterized under the constraints of T_h symmetry. An important deformation of the cage structure is obtained along the D_{2h} distortion path leading to an energy stabilization of 28.5 kcal mol^{-1} with respect to a wave function satisfying the constraints of the T_h point group.[14] Exploratory extended Hückel calculations carried out on V_8C_{12} with the geometry optimized for triplet state 3 of Ti_8C_{12} (T_h symmetry) suggest that a similar situation should occur for the vanadium cluster.

Acknowledgment. All calculations have been carried out on the CRAY-2 computer of the CCVR (Palaiseau, France) through a grant of computer time from the Conseil Scientifique de Centre de Calcul Vectoriel de la Recherche.

Note Added in Proof. After this communication had been accepted for publication, calculations on Ti_8C_{12} and Si_8C_{12} were published by R. W. Grimes and J. D. Gale (*J. Chem. Soc., Chem. Commun.* **1992**, 1222). The calculations, based on the local density approximation, have been carried out on the cage structures with T_h symmetry and the triplet ground state reported for Ti_8C_{12} correlates with state 3 of the present work. The optimized geometrical parameters (C–C = 1.40 Å, M_0–C = 2.57 Å, M_0–Ti = 2.65 Å) are also quite similar to those reported for state 3 in Table I. However, the authors did not consider the FOJT distortion.

Registry No. Ti_8C_{12}, 141344-40-3.

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(10) Another deformation path should be considered by retaining one C_3 axis and the inversion center as unique symmetry elements (S_6 point group). An investigation of this type of distortion with the present basis set is unfortunately beyond our computational capabilities. We intend to carry out a complete exploration of both distortion pathways using a STO-3G basis set. The calculation of the force constants will then indicate whether the optimal geometries belonging to the D_{2h} and S_6 point groups correspond to true distinct minima or not. If negative eigenvalues are generated by the diagonalization of the Hessian matrices, then a conformation with lower symmetry and lower energy is to be found.

(11) Even though the effect of electron correlation has not been investigated in the present study, it can be predicted that the correlation energy of the $4b_{1g}$ and $4b_{2g}$ electron pairs will increase the energy gap in favor of closed-shell state 4.

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(14) Another energy difference of interest should be computed with respect to the *broken symmetry wave function* with lowest energy obtained with a T_h geometry.

Synthesis, Chemistry, and Properties of a Monoalkylated Buckminsterfullerene Derivative, *t*-BuC_{60} Anion

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Although the reactions of lithium and Grignard reagents with buckminsterfullerene (C_{60})[1,2] forming alkylated or arylated products[3] have been reported, no structurally well-defined anionic product has been isolated. The compounds $(R_3P)_2M(\eta^2\text{-}C_{60})$ (M = Ni, Pd, Pt) were 0.36 V harder to reduce than C_{60}, indicating that the electron affinity and reactivity of the C_{60} cluster toward

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