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Silicon-Coated Fullerenes, $(SiC)_n$, n=20 to 60. Preliminary Evaluation of a New Class of Heterofullerenes

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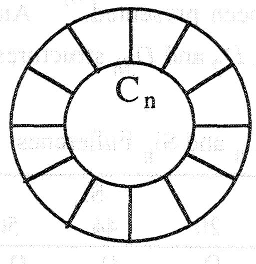
A new approach is proposed to the construction of non-carbon, fullerene-like curved molecular surfaces. A series of saturated, multi-beamed and double-layered structures $(SiC)_n$ (**1**), each consisting of a Si_n sphere enclosing a C_n sphere with Si-C σ-bonds connecting the spheres, are studied by using AM1-SCF-MO method. $(SiC)_{60}$ appears to be the most viable species worthwhile for experimental tests.

Ever-widening and -deepening range of fullerene research[1)] prompts us to expect that strongly curved molecular surfaces like those of fullerenes but made of elements other than carbon should display intriguing properties and behaviors. Except for rare examples,[2)] however, no substantial progress has been achieved in the efforts to produce non-carbon fullerenes.[3)] Carbon is indeed unique in that only this element produces the curled and wrapped clusters upon vaporization by laser ablation or arc discharge. It occurred to us that, instead of searching genuine non-carbon fullerenes, we could use carbon fullerenes as the core material, upon which layer(s) of other elements can be grown taking advantage of the unsaturated nature of core fullerenes. If atomic elements could be bound with the sp^2-hybridized carbon atoms and also with each other on the surface of core fullerene, a sort of beamed and saturated double-layer structure like **1** having exposed and curved surface of the element would result.



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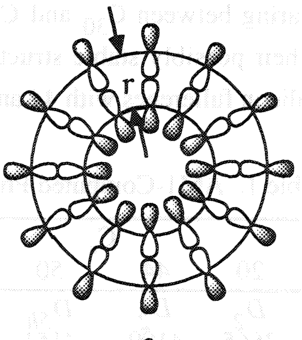

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For the moment, we confine ourselves to those kinds of double fullerenes in which each layer consists of the same number (n) of atoms and surface pattern. The interlayer distance (r, see **2**) must be able to accommodate new σ bonds in order for a structure **1** to be realizable. Suitable elements for the outer layer

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are scanned by geometry-optimizing a few kinds of heterofullerenes and carbon fullerenes C_n, and comparing their radii. Figure 1 shows the results of such calculations for B_n, N_n, and Si_n, as obtained by using AM1 SCF-MO method.4) Fullerenes from B and N produce too narrow interlayer distances to enclose carbon fullerenes having the same number of atoms. However, the radii of Si_n and C_n fullerenes differ by 1 to 2 Å, for n between 20 and 60. Especially noteworthy is the predicted spacing of 1.95Å for n=60, which coincides with the sum of covalent radii of Si and C (1.94 Å). Silicon hence seems to be a promising element for our purpose of coating carbon fullerenes. We describe below the first computational evaluations on silicon-carbon double fullerene model of type **1**.

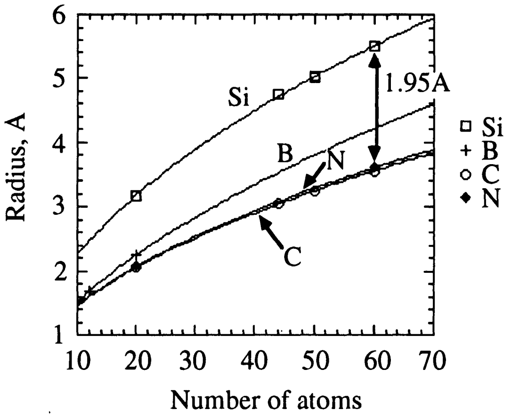


Fig. 1. Change in the radii of fullerenes Si_n, B_n, C_n and N_n with the number of atoms n.

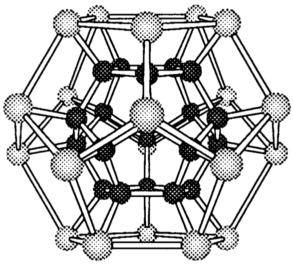
Before discussing the double fullerenes, a brief mention will be given to the single-layered carbon and silicon fullerenes calculated above. Table 1 summarizes the salient features. C_{20} cluster probably does not exist in the form of fullerene,5) but is used in this work as the smallest and quickest test sample. Like I_h-C_{20}6), I_h-Si_{20} proved to have an open-shell electronic configuration and both of them have optimized into close-shell structures with D_2 symmetry by Jahn-Teller distortion. C_{44} and C_{50} are known to be the two prominent fullerenes appearing between C_{30} and C_{60} in the mass spectrum of the product from the laser ablation of graphite, and their possibly stable structures have been presented.6) Among several potential structures for carbon and silicon fullerenes with 44 and 50 atoms, D_2 and D_{5h} structures are found to be the

Table 1. AM1-Computed Properties of C_n and Si_n Fullerenes

	C_n				Si_n			
n	20	44	50	60	20	44	50	60
Point group	D_2	D_2	D_{5h}	I_h	D_2	D_2	D_{5h}	I_h
ΔH_f, kJ/mol	3665	4109	4151	4071	2519	4339	4782	5422
HOMO, -eV	9.14	9.42	9.26	9.64	7.87	7.85	7.70	8.00
LUMO, -eV	3.27	3.58	3.76	2.95	3.49	3.64	3.85	3.38
Bond length, Å								
min	1.408	1.373	1.379	1.385	2.137	2.056	2.066	2.092
max	1.515	1.515	1.492	1.464	2.341	2.340	2.325	2.297

most stable, respectively. C_{60} is naturally the most interesting target to our study, so is Si_{60}.7)

The multi-beamed and double-layered structures **1**, designated here as $(SiC)_n$ (n=20, 44, 50, 60), are 'prepared in computer' by enclosing a C_n within a Si_n fullerene so that the overall point group is kept unchanged, then subjecting the artificial hyperfullerene $C_n@Si_n$ (**2**) to AM1-SCF-MO/geometry-optimization,4) first imposing the respective symmetry constraint but eventually without any constraint. The process spontaneously produce structures **1** from the supermolecule **2**, namely the nearest Si/C pair forms a σ bond and the hybridization of all atoms uniformly changes from sp^2 to sp^3. The first indication of the global change came when it was realized that $C_{20}@Si_{20}$ had changed its symmetry from D_2 to I_h at the end of the



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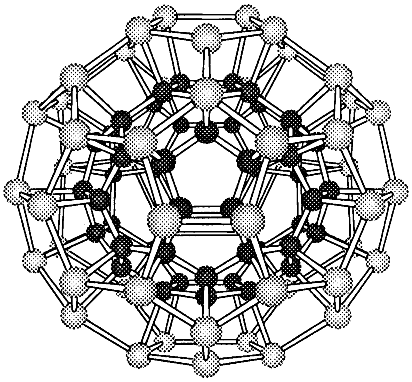

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Table 2. AM1-Computed Properties of $(SiC)_n$

n	20 (**3**)	44	50 (**4**)	60
Point group	I_h	D_2	D_{5h}	I_h
ΔH_f, kJ/mol	4929	5439	5862	6824
$\Delta\Delta H_f$,a) kJ/mol	-1255	-3008	-3067	-2669
HOMO, -eV	8.13	9.08	9.09	9.20
LUMO, -eV	2.66	1.94	1.97	2.05
Av net atomic charge, esu				
C	-0.346	-0.135	-0.112	-0.084
Si	0.346	0.135	0.112	0.084
Av bond length, Å				
C-C	1.498	1.497	1.499	1.503
Si-Si	2.734	2.406	2.365	2.307
Si-C	1.732	1.918	1.950	1.992
Av valence angle, deg				
C-C-C, Si-Si-Si	108.0	114.4	115.1	116.0
Si-C-C	110.9	103.7	102.8	101.6
Si-Si-C	69.1	76.3	77.2	78.4
Bond populationb)				
Si-C	0.685	0.752	0.755	0.760

a) $\Delta\Delta H_f = \Delta H_f[(SiC)_n] - \Delta H_f(C_n) - \Delta H_f(Si_n)$. b) Based on Mulliken population analysis.

calculation - namely the Jahn-Teller effect due to the unfavorable π-electron configuration that was present in initial structure was lifted as the π-orbitals transformed themselves into σ-orbitals to give I_h-$(SiC)_{20}$ (**3**, see also Table 2). The increased C-C and Si-Si bond distances as well as the significant bond populations between the nearest C and Si atoms in the 'double dodecahedron' attest to the conclusion that the structural change from type **2** into **1** indeed occurred (Table 2).

Other $(SiC)_n$'s [n=44, 50 (**4**), 60] retain the original point groups, but here again the multi-beamed and saturated, double-layered heterofullerene structure (**1**) have been confirmed: each of them has a closed electronic configuration with a widened HOMO-LUMO gap, as well as more or less reasonable structural parameters, except for rather small Si-Si-C valence angles for a sp^3-hybridized Si atom. Evolution of net atomic charge in all cases indicates that the new Si-C single bonds are polarized. It is noteworthy that all the $(SiC)_n$'s examined in this work have lower heats of formation compared to the sum of the heats of formation for the component Si_n and C_n fullerenes ($\Delta\Delta H_f$ in Table 2). Although heats of formation obtained by the AM1 method is known to deviate substantially from the experimental values,[8] $\Delta\Delta H_f$ values shown in Tab. 2 should suffer less from this disadvantage due to substraction of similar quantities. Although heats of formation obtained by the AM1 method is known to deviate substantially from the experimental values,[4a] $\Delta\Delta H_f$ values shown in Tab. 2 should suffer less from this disadvantage due to substraction of similar quantities. The present result suggests that the formation of inherently strong Si-C bonds would override the high geometrical strain present in **1**. Among the hypothetical heterofullerenes given in Table 2, $(SiC)_{60}$ appears to be the most favorable candidate for an experimental verification, which is being planned.

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