# New Surface Allotropes of Carbon

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**Abstract**

The simplest negatively curved (schwartzene) surface allotrope of carbon, $C_{32}$-trousers, is introduced and modeled. Restricted Hartree-Fock calculations show that $C_{32}$-trousers is a stable unit and also demonstrate the viability of several related schwartzenes. In contrast to many schwartzene structures proposed earlier, $C_{32}$-trousers is a reasonable target for organic synthesis.

Familiar forms of pure carbon are the lattice allotrope, diamond, and the surface allotrope, graphite. Within the past decade, attention has focused on surface allotropes of carbon having positive curvature and spherical topology (fullerenes) with pentagonal rings, most notably $C_{60}$, buckminsterfullerene, which has been synthesized and studied[1,2]. More recently, the class of surface allotropes has been enriched by consideration of cylindrical tubules[3], as well as more speculative examples (the schwartzenes) with more complicated topology involving negative curvature, requiring many heptagonal rings of carbon[4–9]. In this paper we investigate the simplest fundamental building unit for schwartzene surface allotropes, $C_{32}$-trousers. An interesting molecule itself, $C_{32}$-trousers also may be used to join tubules into systems of “bucky-plumbing” or assembled into periodic schwartzite structures[4,6,7] with high moduli of elasticity and low density.

We define a molecule to be a surface allotrope whenever one can find a smooth surface passing through all the atomic nuclei, such that the electron density decreases locally as one moves normal to this surface. This concept is implicit in much of the previous work on carbon allotropes. A carbon surface allotrope will necessarily have each atom bonded to 3 neighbors; however this local combinatorial requirement is not sufficient to characterize a surface allotrope. For example, the structure in Figure 3a depicts an allotrope composed entirely of trivalent carbons that is not a surface allotrope.

An important topological invariant of a surface is its Euler number $\chi$, which for a closed or periodic surface determines the topology. For example, $\chi = 2$ characterizes a sphere, while $\chi = 0$ for a torus or cylinder (which can be viewed as the plane with suitable doubly- or singly-periodic identifications). If such a surface is tessellated with a network of hexagons, pentagons and heptagons, then it has been noted[5] the numbers $p$ and $h$ of pentagonal and heptagonal rings on the surface must satisfy the Euler relation $p - h = 6\chi$. The Gauss-Bonnet formula implies that the total curvature of the surface is $2\pi\chi$. Flat, doubly-periodic graphite can be viewed as an unwrapped torus, hence only hexagons are needed. Positively curved surface allotropes will have an excess of pentagons, while negatively curved allotropes have an excess of heptagons. Trousers (see Figure 1) are topologically the most basic negatively curved surface, with $\chi = -1$. Surfaces of every topological type (besides the plane, sphere or cylinder) can be built from trousers. It is possible to make a tessellation of a trousers surface with exactly 6 heptagons and no hexagons. The resulting surface allotrope ($C_{26}$-trousers) fails to satisfy the classical double-bonding rules, however, and does not appear to yield a stable molecule. The simplest stable trousers surface allotrope of carbon satisfying the classical rules of valence is $C_{32}$-trousers consisting of 6 heptagons and 3 hexagons.

Quantum mechanical modeling at the restricted Hartree Fock (RHF) level using the AM1 semiempirical molecular orbital (MO) method yields the symmetric molecule shown in Figure 2. Since we are not carrying out computations on infinite networks of carbons with periodic symmetry, we terminated all unfulfilled carbon valences with C-H bonds. For example, $C_{32}$-trousers is computed using a $C_{32}H_{12}$ molecule. The presence of these C-H bonds will be implicit in our discussions, so we shall refer to our surface allotropes as being molecules of general structure $C_n$.

Unconstrained RHF-AM1 MO computations readily optimized to the $D_{3h}$ structure of $C_{32}$-trousers. Bond lengths, Mulliken bond orders, and some important bond angles obtained from the optimization are summarized in the Table. There was no distortion, as has been computed for some carbon clusters that have non-singlet ground states[10]. (As a test of the methodology, we also optimized the structure of $C_{60}$-buckminsterfullerene, by RHF-AM1 and found agreement with the structures previously computed by semiempirical MO methods[10] and with the experimental structure. For our $C_{60}$-buckminsterfullerene structure, $r_{C-C} = 1.385$ and $1.464$ Å, while the experimental values are estimated[11] to be $1.40 \pm 0.015$ and $1.45 \pm 0.015$ Å by solid state

$^{13}$C nuclear magnetic resonance spectroscopy.)

The atoms along the three-fold rotation axis of $C_{32}$-trousers, while nominally of $sp^2$ hybridization, are actually pyramidalized. The resultant $C_2C_1C_7$ angle is only 116.8°, and the plane tangent to $C_1$ and equidistant from carbons $C_2, C_7$, and $C_8$ makes a pyramidalization angle of 15.4°. The central carbon $C_1$ is joined to the peripheral carbons by bonds of 1.46 Å, which have RHF-AM1 bond orders of 1.22. These bonds are longer and weaker than the C=C bond of benzene, 1.395 Å and a bond order of 1.42.

The $C_4C_5$-bond and its five symmetry equivalents on the trousers periphery all have bond lengths of 1.35 Å and bond orders of 1.91. These values are similar to the RHF-AM1 values for ethylene, 1.326 Å and 2.00, respectively. Localization of bonding in these positions does not appear to be an artifact of the valence-terminating hydrogen atoms, since we find similar bond lengths in the extended structures[12] shown in Figure 3. For instance, in the RHF-AM1 optimized structure of $C_{60}$-trousers dimer, the central bond corresponding to the $C_4 = C_5$ bond in $C_{32}$-trousers has a bond length of 1.38 Å and a bond order of 1.77.

The set of six equivalent transannular bonds $(C_3 - C_{\bar{3}}, \ldots)$ all have bond lengths of 1.40 Å and bond orders of 1.58, and so are computationally similar to those of benzene, despite the pyramidalization of the $sp^2$ carbons involved. Molecules with similarly pyramidalized $sp^2$ carbons are well known[13]. For instance $9, 9'$-didehydrodianthracene is stable at room temperature[14]. The computed structural parameters for $C_{32}$-trousers are within normal limits for bonding of stable molecules. We therefore see no structural reason why materials containing $C_{32}$-trousers would not be viable, although they may be reactive or difficult to synthesize.

For example, $C_{60}$-trousers dimer (Figure 3b) and $C_{56}$-diamond trousers (3c) are the basic units for building doubly and triply periodic schwartzites respectively. Scuseria has suggested more elaborate $D_{3h}$ schwartzenes as well as some with tetrahedral symmetry[9]. The simplest schwartzene unit with $T_d$ symmetry is our $C_{52}$ depicted in Figure 3e, comprising twelve heptagons only.

Because its relative simplicity (compared to earlier proposed structures[4−10,15]) should compensate for its additional strain energy, $C_{32}$-trousers is a target for rational organic synthesis. In addition, schwartzites and tubule-containing surface allotropes based upon $C_{32}$-trousers may yet be discovered among the increasingly rich variety of carbon allotropes[16].

# Endnotes


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Table. RHF-AM1 bonding parameters[*].

| Compound | Parameter[†] | Value[‡] | Bond Order[§] |
|---|---|---|---|
| $C_{32}H_{12}$ | $C_4C_5$ | 1.349 | 1.91 |
| | $C_2C_3$ | 1.455 | 0.98 |
| | $C_1C_2$ | 1.460 | 1.22 |
| | $C_3C_{\bar{3}}$ | 1.401 | 1.58 |
| | $C_2C_1C_7$ | 116.8° | |
| | $C_3C_2C_9$ | 106.8° | |
| | $C_2C_3C_{\bar{3}}$ | 111.8° | |
| | $C_3C_4C_5$ | 113.4° | |
| $C_{60}$[‖] | $(C-C)\, r_1$ | 1.464 | 1.10 |
| | $(C-C)\, r_2$ | 1.495 | 1.50 |
| ethylene | $C=C$ | 1.327 | 2.00 |
| benzene | $C-C$ | 1.395 | 1.42 |

[*]Computations were carried out using the SPARTAN computational chemistry software package (Wavefunction Inc., Irvine, CA version 3.1) implemented on a Silicon Graphics Indigo R4000 workstation. Initial structures were optimized using the MM2 force field included in SPARTAN. [†]See the numbering scheme of Figure 2 for $C_{32}$ trousers. [‡]Lengths in angstroms ($\AA$), angles in degrees (°). [§]Mulliken RHF-AM1-SCF bond order. [‖]Buckminsterfullerene.

Figure 1. Tesselated trousers surface.

Figure 2. Stereographic view of RHF-AM1 optimized $C_{32}$-trousers. Open circles represents hydrogens used to terminate the twelve unsatisfied valences of $C_{32}$. Visualizations of structures were carried out using the QUANTA 4.0 program (Molecular Simulations Inc., Burlington, MA).

Figure 3. Views of schwartzite units and partial structures. a) Lattice allotrope composed of trivalent carbons (stereo pair) b) $C_{60}$-trousers dimer, $D_{2h}$ symmetry. c) $C_{56}$-diamond trousers, $D_{2d}$ symmetry. d) $C_{52}$ unit, $T_d$ symmetry (stereo pair) e) Part of network containing $C_{32}$-trousers. f) $C_{32}$-trousers-based nanocog.