Gold Fullerenes

Au_{32}: A 24-Carat Golden Fullerene[**]

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For more than a decade, gold nanostructures have attracted the attention of experimentalists and theoreticians alike. Recent years have witnessed increased interest in gold-containing structures, as several fields of application have found the metal to be not only aesthetical, but also of practical use.[1] In contrast to carbon where the familiar buckminsterfullerene[2] came first, later to be followed by carbon nanotubes, gold research started in reverse; gold nanotubes are already a synthetic reality.[3] Au_{32} has to date been considered a moderately uninteresting molecule, just one among the many gold clusters. The most stable structure has been suggested to be space-filling,[4,5] like the majority of all metal clusters studied to date. Using relativistic quantum chemical calculations, we show the existence of another stable isomer: the icosahedral "golden" fullerene Au_{32}, the first all-gold fullerenic species. It is spherical and hollow (with a diameter of ≈ 0.9 nm) and structurally very similar to C_{60}. Au_{32} has a record value of magnetic shielding at its center, and appears to be aromatic.

Considering its place in the periodic table, gold is an unusually relativistic element.[6] Among other things, this is expressed in its bonding properties. The element manifests aurophilicity, which further enhances the strong gold–gold interactions.[7] Relativistic effects make many interesting pure gold species such as clusters and nanotubes possible. In addition, heterogenic species are also studied with great interest. The bimetallic icosahedron WAu_{12}, first predicted by Pyykkö and Runeberg[8] and later synthesized by Li et al.,[9] is representative of these. Recently, images of multiwalled gold nanowires were published.[3] No reports of pure "golden" fullerenes exist, however. The closest match is WAu_{12}, where the Au_{12} shell engulfs a tungsten atom. The icosahedral form of Au_{12} is itself, however, unstable.[10]

Few studies of Au_{32} exist. Work with empirical potentials suggest that the global energy minimum for the molecule is a low-symmetry, lumplike structure of either C_2[4] or D_2 symmetry.[5] The scalar relativistic density functional theory (DFT) calculations presented here show that Au_{32} has another minimum: the icosahedral fullerenic form. To determine the stability of the Au_{32} fullerene, we first optimized its structure. Two different functionals, the popular generalized gradient approximation (GGA) functional BP86[11] and the nonempirical hybrid GGA functional PBE0,[12] were used throughout this work. Au_{32} is composed of triangles in icosahedral symmetry, making a near perfect rhombic triacontahedron. Each atom binds to either five or six neighboring gold atoms. Thus, the symmetry is the same as for the truncated icosahedron C_{60}, with the vertices and planes interchanged. Figure 1 shows the structure of Au_{32}, compared with C_{60}.

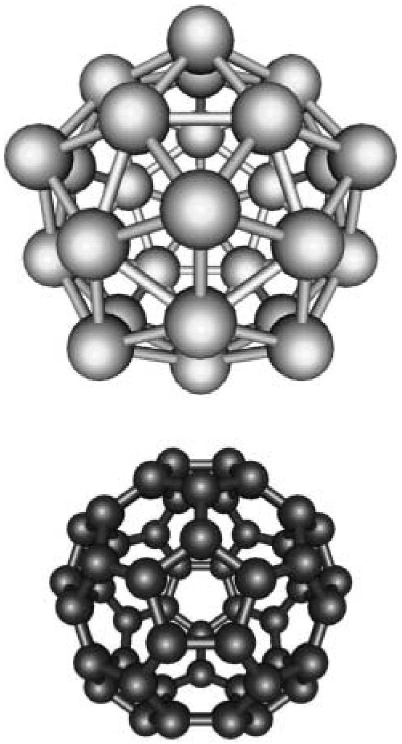

Figure 1. The molecular structures of the Au_{32} (above) and C_{60} (below) fullerenes. The calculated Au–Au bond lengths vary between 276 and 287 pm. The figure was prepared using the gOpenMol package.[32]

Au_{32} is a closed-shell molecule with an appreciable energy gap between the frontier orbitals, factors important for stability. The gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is 1.7 and 2.5 eV as calculated with the BP86 and PBE0 functionals, respectively. The high symmetry of the molecule increases the density of states in the frontier orbital region; both the HOMO and LUMO are fourfold degenerate.

The harmonic vibrational frequencies of the optimized molecular structure show the icosahedral form to be a minimum; no imaginary frequencies were obtained. A stationary point on the potential energy surface (PES) does not

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ensure that other conformations lower in energy do not exist, however. We compared the energy of the Au_{32} fullerene to the structures suggested previously. The energy difference is surprisingly large in favor of the fullerenic form. With the BP86 functional, the difference is $150\,kJ\,mol^{-1}$ to the C_2 structure and $182\,kJ\,mol^{-1}$ to the D_2 structure. The hybrid PBE0 functional yields a slightly smaller energy difference: 79 and $123\,kJ\,mol^{-1}$ against C_2 and D_2, respectively. The cohesive energy of Au_{32}, based on the computed energies of Au_2 and Au_{32}, and the experimental dissociation energy of Au_2[13] and the cohesive energy of bulk gold,[14] is 60 % of the bulk value. As noted by Adamo and Barone, PBE0 is arguably the best available functional for dispersion forces,[12b] without parameters fitted to experimental data. These energetics should thus be the most reliable that DFT can provide. However, none of the existing functionals are optimal for evaluating the largely dispersion-based aurophilic contribution. An underestimation of gold–gold interactions could artificially raise the energy of bulk gold compared to the fullerene. Also, it has been shown that DFT slightly overestimates the stability of planar gold structures.[15a] Therefore, it cannot be concluded with absolute certainty that the fullerenic form is the true global minimum of Au_{32}, only that it is quite stable.

The stability of Au_{32} seems strongly rooted in relativistic effects. The valence isoelectronic "silvery" fullerene, Ag_{32}, is already higher in energy than space-filling isomers, by at least $100\,kJ\,mol^{-1}$ (PBE0). As shown by Furche, Häkkinen, and coworkers,[15] relativity makes the preference for planar structures over 3D structures much more pronounced for gold than for silver. We also compared the stability of Au_{32} to the intriguing Au_{20} tetrahedral cluster, recently reported by Wang and co-workers.[16] As expected, the stability of Au_{32} is higher than that of Au_{20}, by 10 and $7\,kJ\,mol^{-1}\,atom^{-1}$ at the BP86 and PBE0 levels, respectively. In Table 1, we compare other calculated properties of the two highly symmetric gold clusters. C_{60} is included for comparison. Many similarities among the molecules can be noted.

Another factor stabilizing Au_{32} is aromaticity. Strong nuclear magnetic shielding effects in areas lacking electron density, like the center of fullerenes, is an indication of induced ring currents in a molecule.[17] This in turn correlates strongly with aromaticity. The negative of the magnetic shielding at the center of the cage equals the nucleus-independent chemical shift (NICS) value,[18] a popular method for assessing the degree of aromaticity; in general, the more negative the NICS, the stronger the aromaticity. Our magnetic shielding calculations show that the induced currents of Au_{32} are stronger than those of C_{60} and its ions. Up to now, the centers of the C_{60}^{10+} and C_{80}^{8+} ions have held the record for the largest predicted diamagnetic shielding (≈ 80 ppm).[19] The shielding at the center of the neutral Au_{32} cluster is even stronger (≈ 100 ppm). At least two factors can explain this huge shielding. First, Au_{32} has seven times the number of electrons as C_{60}. And second, when the aromatic character is assumed to be accrued by the 32 6s electrons of gold, the $2(N+1)^2$ rule for spherical aromaticity[19] is fulfilled, with $N=3$. The neutral C_{60} does not fulfill this rule, and indeed shows only a moderate shielding effect. C_{60}^{10+}, on the other hand, is spherically aromatic. Figure 2 shows the magnetic shielding along a line from the centers of Au_{32} and C_{60}^{10+}. Both are seen to behave like miniature magnetic Faraday cages; the shielding inside the spheres is nearly constant. Using the magnetic criterion, Au_{20} is also aromatic. We note that the aromaticity of planar gold compounds has been suggested before.[20]

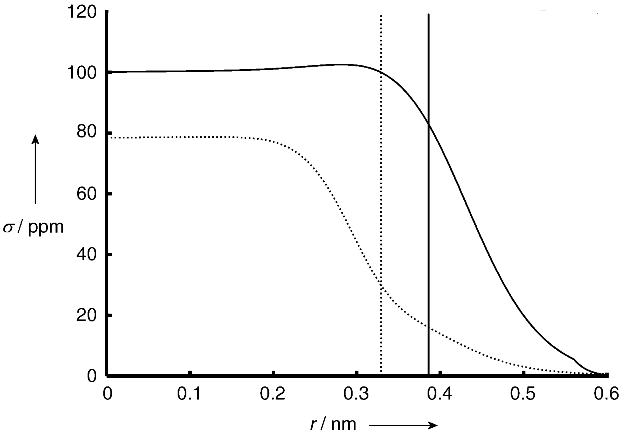

Figure 2. The magnetic shielding σ (in ppm) along a line from the centers of Au_{32} (——) and C_{60}^{10+} (-----). The Au_{32} line goes through the midpoint of a triangle. The C_{60}^{10+} line goes through the midpoint of a hexagon; the line through a pentagon (not shown) is almost identical. The vertical lines indicate the distance of the corresponding midpoints from the centers, which equate approximately to the radii of the molecules.

Table 1: Calculated properties of Au_{32}, Au_{20}, and C_{60}.

Property	Au_{32}	Au_{20}	C_{60}
Diameter [nm][a]	0.9	0.7	0.7
Symmetry point group	I_h	T_d	I_h
HOMO–LUMO gap [eV]			
BP86/PBE0	1.7/2.5	1.9/3.1	1.6/3.0
Frontier orbital config.	$(t_{2u})^6(g_u)^8(g_g)^0$	$(t_2)^6(e)^4(t_2)^0$	$(g_g)^8(h_u)^{10}(t_{1u})^0$
Degeneracy of HOMO/LUMO	4/4	2/3	5/3
Vibrational freq. [cm^{-1}]			
lowest, BP86/PBE0	30/37	28/18	257/273
highest	145/147	172/184	1560/1674
NICS at center of cage, BP86	−100	−36	−2[b]

[a] Approximate values. [b] For C_{60}^{10+}, the corresponding NICS value is −78.

The stable gold triangles seem to be ideal building blocks for a variety of molecular-sized geodesic domes, other all-gold fullerenes. Au_{32} is structurally similar to C_{60} in that it can be constructed using the carbon fullerene as a template. By replacing the midpoints of the pentagons and hexagons by 32 gold atoms and then discarding the carbon atoms, one is left with a good model of Au_{32}. Following the same procedure for C_{20} leads to the spherical Au_{12} (which is unstable by itself). Further, by using C_{80} as a template, the icosahedral Au_{42} is obtained, and so on. By not just deleting the carbon atoms of C_{60} after inserting the 32 gold atoms at the centers of the rings, but instead replacing them by gold atoms (and stretching the bonds appropriately), one arrives at Au_{92}. Its icosahedral fullerenic form, with a diameter of ≈ 1.5 nm, would need an overall -6 charge to fulfill the spherical aromaticity rule and have a filled HOMO. Gold is highly electronegative, so this charge, especially if donated by electropositive species, is plausible. DFT cannot, however, routinely treat highly charged anions. Preliminary calculations on the closest cation with a filled HOMO, Au_{92}^{2+}, show that it is metastable. At the BP86 level, it is a stationary point on the PES, lower in energy than the corresponding planar gold sheet, but higher in energy than space-filling clusters. Au_{92} could readily be filled with another species. In analogy with nested nanotubes, an obvious thing to insert into Au_{92} would be Au_{32}. They seem to be a perfect match; the distance between the shells would be about 280 pm. The diameter of the fullerenic Au_{32}, about 0.9 nm, matches the most common diameter of the stable nanotubes reported by Kondo and Takayanagi.[3] This suggests that Au_{32} and other "golden" fullerenes might be synthesizable by cutting a nanotube of appropriate size, with accompanying closure of the ends.

A wide range of future uses for the "golden" fullerenes can be imagined. Being hollow, they could be used as nanoshells more versatile than the normal, fixed-core variety.[21] The hollow cavity of the fullerenes offers more flexibility than what can be achieved with space-filling particles. Of course, as with other nanoparticles, the outside of the fullerenes could also be capped with auxiliating ligands. Gold fullerenes could find use as transporters for small molecules, perhaps distributing pharmaceuticals and other chemicals in the human body; gold nanoparticles are for example attachable to certain viruses,[22] and can even enter cell nuclei.[23] Decomposition in the body would be harmless, and would enable many other biomedical applications.[24] A less ambitious but related use would be to use "golden" fullerenes for labeling purposes.[25] Various fillings and dopants could tune detectable properties of the clusters. In particular, the huge magnetic shielding at the center of Au_{32} should prove useful.

We have shown that Au_{32} in its fullerenic form is a chemically robust molecule. We hope that our work will inspire the realization of the "golden" fullerenes, not only through computational studies like those reported here, but also in a traditional test tube.

Methods

The molecular structures of the species studied were calculated at the density functional theory (DFT) level using the gradient-corrected functional BP86[11] and the hybrid, nonempirical functional PBE0.[12] Where possible, the efficient resolution of the identity (RI) approximation[26] was employed. Most properties were calculated with the TURBOMOLE[27] program suite, version 5.6, with the polarized quadruple-zeta basis set VQZPP which includes three *f*-functions. The standard grid size denoted m4 was used. Frequencies were calculated numerically using NUMFORCE. The PBE0 energy comparisons between Au_{32} isomers were calculated on structures optimized with the TZVPP(2f) triple-zeta quality basis set. Calculations on the silver and carbon fullerenes used the standard TZVPP basis sets. The magnetic shielding calculations were made using the individual gauges for localized orbitals (IGLO) method,[28] with a modified version of the DEMON package,[29] using a (6s5p3d) valence basis set, on the BP86/TZVPP(2f)-optimized structures. For Au_{32}, a three-group orbital localization was necessary. The shielding calculations on C_{60} used the ECP-MWB-DZP basis set and the ECP-MWB-4VE ECP.[30] All shielding calculations were made at the BP86 level. The Stuttgart 60- and 28-electron effective core potential (ECP)[31] modeled the scalar relativistic effects of Au and Ag, respectively. The basis set definitions are detailed in ref. [10].

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