Fullereneynes: a new family of porous fullerenes

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We propose a new family of C_n cage molecules which have the same highest possible symmetry of I_h and the same number of sp^2 carbon atoms as either C_{60} or related larger fullerenes, but in addition contain sixty or more sp-bonded carbon atoms. The cages of these fullereneynes are porous, which should facilitate the reversible formation of endohedral compounds, as well as complexes in which dopants reside in the cluster shell. We determine the optimized geometries and formation energies of two prototypical examples, namely the C_{120} and C_{180} molecules, using a tight-binding Hamiltonian which has been applied successfully to large carbon clusters. The C_{120} and C_{180} fullereneynes are expected to be stable despite a binding energy which is about 1 eV per atom lower than for graphite. Moreoever, the per atom binding energy dramatically increases with increasing size of fullereneynes containing equal number of sp^2 and sp carbon atoms and approaches a value which is only 0.2 eV/atom lower than for the C_{60} fullerene.

The relatively recent bulk synthesis [1] of C_{60} clusters with the "hollow soccer ball" (or "fullerene") structure [2] has triggered enormous scientific and public interest in this new form of carbon. A whole plethora of carbon-only structures has emerged from world-wide research effort, ranging from very large carbon fullerenes [#1] to "bucky tubes" [4]. An important branch of the new fullerene chemistry are endohedral complexes $A@C_n$ with an atom A or a small atomic cluster inside. Such complexes have been formed only during fullerene syntheses or during highly energetic post-synthesis processes [5], since there is an enormous activation barrier for the penetration of atoms through the carbon rings of C_{60} or related fullerenes. In contrast, fullerene-like molecules with a "porous" surface are likely candidates for materials which undergo an easily reversible formation of endohedrals.

In this Letter, we investigate the structure and properties of a family of such hypothetical molecules, the fullereneynes. These carbon cluster molecules are named fullereneynes, since they contain the same number of sp^2 carbon atoms and (neglecting a possible Jahn–Teller distortion) have the same I_h symmetry as their parent fullerene, but also contain triple bonds ("yne" groups). The number of sp carbon atoms is one, two, or three times the number of sp^2 carbon atoms. The heuristic process which leads from a fullerene of symmetry I_h to these different fullereneynes having low strain energy can be understood by labeling bonds in the fullerene as either nominal "single bonds" or nominal "double bonds". The nominal single and double bonds in the C_{60} fullerene are those within the pentagons and radial to pentagons, respectively. The bonds in the higher fullerenes are uniquely labeled for topological purpose as either "single bonds" or "double bonds" according to the valence bond structure which results from assigning bonds on the pentagonal ring as "single bonds", allowing only hexagonal rings with either all single or three "single" and three "double" bonds, and constraining the symmetry to I_h. Starting from a C_m fullerene of symmetry I_h, the C_{2m}, C_{3m} and C_{4m}

[#1] Synthesis and topology of large fullerenes has been reviewed by Curl and Smalley [3].

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fullereneynes result from the heuristic process of inserting C(sp)C(sp) linkages in either all of the bonds labeled as "double bonds", all of the bond labeled as "single bonds", or in all bonds in the fullerene. The resulting structures have combinations of $(C(sp^2)C(sp)C(sp)C(sp^2))_3$ rings and unchanged phenyl rings for the C_{2m} fullereneynes, $(C(sp^2)C(sp)C(sp)C(sp^2))_3$ rings and $(C(sp^2)C(sp)C(sp))_6$ rings for the C_{3m} fullereneynes, and only $(C(sp^2)C(sp)C(sp))_6$ rings for the C_{4m} fullereneynes, in addition to the pentagonal rings.

We used a parameterized tight-binding formalism to determine the optimized geometries and the binding energies of the C_{120} and C_{180} structures [6]. This method has previously been used successfully to determine the relative stabilities of large carbon clusters [6]. For maximum accuracy, one would of course prefer an ab initio scheme, such as the density functional approach [7]. The geometry optimization of the large fullereneynes, however, requires more computer-efficient methods and a high quality ab initio treatment is out of question at this point.

We write the binding energy of a fullereneyne cluster (with respect to isolated atoms) as a sum of five terms [6],

$$-E_{\mathrm{coh}} = \sum_{\alpha} n_{\alpha}\epsilon_{\alpha} + \sum_{i<j} E_{\mathrm{r}}(d_{ij}) + \sum_{i} \psi(Z_i) + U\sum_{i=1}^{n} (q_i - q_i^0)^2 - nE_{\mathrm{tot}}(\mathrm{C\,atom})\,. \qquad (1)$$

Here, the electronic states are labeled by α and the atomic sites by i, j. The first term in eq. (1) is the one-electron energy of the cluster, where ϵ_α are the eigenvalues of a Slater–Koster parameterized [8] Hamilton matrix and n_α are the corresponding occupation numbers. The second and third term describe the repulsion in the cluster which is dominated by the pairwise internuclear and closed-shell repulsion, but also contain terms arising from electronic "overcounting" and exchange-correlation energies. E_{r} and ψ parameterize the repulsive energies as pairwise interactions which depend on the nearest-neighbor distances d_{ij} and the nearest-neighbor coordination numbers Z_i. The fourth term is an intra-atomic Coulomb repulsion arising from possible charge transfers between inequivalent sites. The last term is the reference energy of isolated neutral carbon atoms.The parameters used in eq. (1) have been obtained from a global fit to local density approximation [7] calculations for the electronic structure of C_2, a graphite monolayer, and bulk diamond for different nearest-neighbor distances, and have been given in ref. [6]. Zero-point vibrational energies are neglected in our binding energy expression.

The C_{120} and C_{180} fullereneynes, if constrained by the I_h symmetry, both have only two inequivalent carbon sites and four degrees of freedom to place the atoms on the ball (see figs. 1b and 1c). In the C_{120} molecule, the carbon "double bonds" of C_{60} (defined above, see fig. 1a) have been replaced by $C(sp^2)C(sp)C(sp)C(sp^2)$ linkages. These new edges of the fullereneynes are characterized by the $C(sp^2)C(sp)$ bond length d_1 and the corresponding C(sp)C(sp) bond length d_2. Moreover, the two C(sp) atoms are free to move in the radial direction. We describe the radial position of these atoms by the

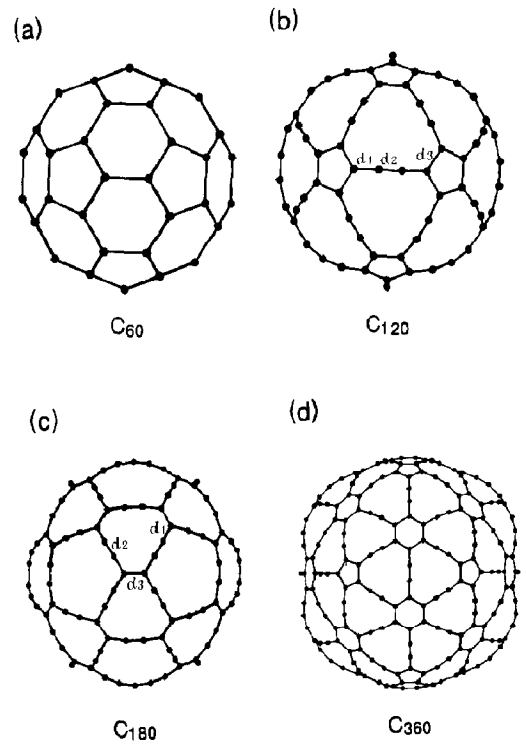

Fig. 1. Twofold axis projections for (a) the C_{60} fullerene, (b) the C_{120} fullereneyne, (c) the C_{180} fullereneyne, and (d) the C_{360} fullereneyne.

bending parameter $\beta = R(C(sp))/R(C(sp^2))$, where R is the distance of an atom from the ball center. The last free parameter is the $C(sp^2)C(sp^2)$ bond length d_3, which originates from the "single bonds" in the C_{60} structure (bonds in the pentagons, see fig. 1a).

In the C_{180} molecule, the carbon "single bonds" of C_{60} have been replaced by $C(sp^2)C(sp)C(sp)C(sp^2)$ linkages. All structural parameters are defined in analogy to the C_{120} fullereneyne.

We used the energy expression in eq. (1) to optimize the four parameters characterizing the structure of the C_{120} and C_{180} fullereneynes. Based on the finite increments in d_1, d_2, d_3, and β used for energy minimizations, the optimized bond lengths are expected to be accurate to ± 0.05 Å and the β parameter to ± 0.002. The size of these estimated errors must be judged in view of the large number of degrees of freedom and the complexity of the systems. For the C_{120} molecule, the optimum structure is given by $d_1 = 1.32$ Å, $d_2 = 1.21$ Å, $d_3 = 1.33$ Å, and $\beta = 0.967$, corresponding to an almost spherical cluster shape. The effective radius of the fullereneyne lies between $R(C(sp)) = 5.41$ Å and $R(C(sp^2)) = 5.60$ Å. The binding energy per atom (with respect to isolated atoms) is $E_{coh} = 6.39$ eV, almost 1 eV less than for graphite, $E_{coh} = 7.37$ eV, and substantially less than for the C_{60} fullerene, $E_{coh} = 6.99$ eV [6]. These relatively low binding energies are caused by the large number of sp carbon atoms. The C(sp) atoms carry a negative Mulliken charge of -0.03 e, which is compensated by a positive charge of $+0.03$ e on the $C(sp^2)$ atoms. The C_{120} molecule has a fourfold degenerate highest occupied molecular orbital (HOMO) and a fivefold degenerate lowest unoccupied molecular orbital (LUMO). These degeneracies are, of course, given by the symmetry of the molecule and the connection topology, and independent of the exact geometry. The HOMO–LUMO gap in this symmetric structure is small, only 0.11 eV. We find the HOMO to be occupied by only six electrons. A small energy gain is expected in this situation from a Jahn–Teller distortion, which would split the degeneracy of the HOMO by lowering the symmetry of the fullereneyne.

The optimum structure of the C_{180} molecule is given by $d_1 = 1.33$ Å, $d_2 = 1.20$ Å, $d_3 = 1.33$ Å, and $\beta = 0.988$, corresponding to an almost spherical cluster shape. The effective radius of this fullereneyne lies between $R(C(sp)) = 7.23$ Å and $R(C(sp^2)) = 7.32$ Å. The binding energy per atom (with respect to isolated atoms) is $E_{coh} = 6.24$ eV, close to the value found for the C_{120} fullereneyne. The C(sp) atoms carry a negative charge of -0.07 e, which is compensated by a positive charge of $+0.14$ e on the $C(sp^2)$ atoms. The C_{180} molecule has a fourfold degenerate HOMO, a threefold degenerate LUMO, and a HOMO–LUMO gap of 0.21 eV. As in the symmetric C_{120} molecule, the HOMO is partly occupied by only two electrons. Again, we expect a small energy gain to arise from a Jahn–Teller distortion, which would split the degeneracy of the HOMO by lowering the molecular symmetry.

In order to obtain an independent estimate of the bond lengths in the fullereneynes, we performed a valence bond analysis starting from experimentally determined bond lengths for model compounds [9,10]. Our analysis uses $d(C(sp^2)–C(sp^2)) = 1.455$ Å, $d(C(sp^2)–C(sp)) = 1.434$ Å, $d(C(sp^2)=C(sp^2)) = 1.331$ Å, $d(C(sp^2)=C(sp)) = 1.307$ Å, $d(C(sp)=C(sp)) = 1.282$ Å, and $d(C(sp)\equiv C(sp)) = 1.189$ Å. Slightly different bond length values were obtained by either equally weighing all 12500 valence bond structures (which is the same number of valence bond structures as for C_{60} [11]) or by averaging over only the lowest energy class of such structures. The values obtained by these two methods for the C_{120} fullereneyne are $d_1 = 1.378$ and 1.409 Å, $d_2 = 1.230$ and1.208 Å, and $d_3 = 1.420$ and 1.405 Å, respectively. Likewise, the values obtained for C_{180} are $d_1 = 1.398$ and 1.434 Å, $d_2 = 1.215$ and 1.189 Å, and $d_3 = 1.400$ and 1.331 Å, respectively. In light of the expected higher energy of valence bond structures having a greater fraction of butatriene linkages, the latter bond length value in each linked pair is preferred. The typical differences between these bond lengths and those calculated using eq. (1) are smaller than 0.1 Å.

As mentioned above and illustrated in figs. 1 and 2, the fullereneynes could function as porous balls which permit the reversible formation of endohedral complexes. With the van der Waals radius of $R_{vdW} = 1.7$ Å for carbon atoms, the van der Waals radius of the central void is 3.7 Å for C_{120}, and the largest hole on the C_{120} surface has a van der Waals radius of 0.2 Å. Both C_{120} and C_{180} have twenty such holes. This hole radius is sufficiently large for the

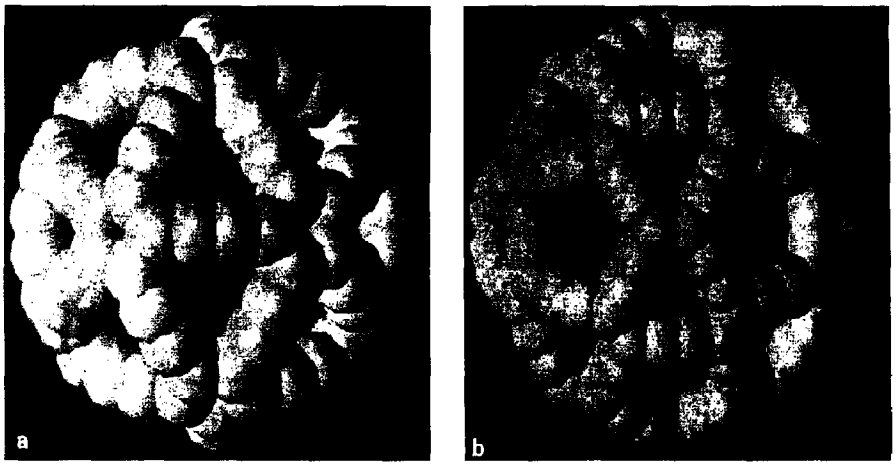

Fig. 2. Pictures of space-filling models for (a) the C_{120} and (b) the C_{180} fullereneyne molecules. For clarity, the carbon atoms are represented by spheres with a radius of 1.1 Å, as compared with a van der Waals radius of 1.7 Å for carbon atoms.

thermally activated diffusion of small ions such as Li^+ (van der Waals radius of 0.60 Å). For C_{180}, the van der Waals radius of the central void is 5.5 Å, only slightly larger than the exterior van der Waals radius of the C_{60} molecule (5.2 Å). This near perfect onion-like size match suggests a possible synthesis path for the C_{180} molecule on a C_{60} substrate. The largest hole on the C_{180} surface has a van der Waals radius of 1.0 Å, and there are twelve such holes centered on the pentagonal rings. The largest holes in C_{180} are sufficient to permit easy diffusion of H_2 and the ions of many elements.

Neglecting molecular strain contributions and resonance stabilization, the gas-phase heats of formation of C_{120} and C_{180} can be calculated by the group increment method, using observed heats of formation for model compounds. These calculations used group increments developed for graphynes, proposed planar carbon phases involving sp carbons [9]. The resulting calculated gas-phase heats of formation (with respect to graphite), evaluated for the lowest energy class of valence bond structures, are 24.4 kcal/mol carbon for C_{120} and 23.7 kcal/mol carbon for C_{180}. Using a binding energy of 7.37 eV/atom for a graphite monolayer, these results provide a cohesive energy of 6.31 eV/atom for C_{120} and 6.34 eV/atom for C_{180}, in very good agreement with the results of the present tight binding calculations. The above heats of formation are slightly less than the similarly calculated [9] gas-phase heat of formation for linear carbon, $(-C{\equiv}C-)_n$, which is 25.4 kcal/mol carbon (corresponding to a cohesive energy of 6.27 eV/atom). The heats of formation of the higher fullerenes with I_h symmetry approach that of a graphite monolayer (1.5 kcal/mol carbon). In the same sense, the heats of formation of the C_{2m}, C_{3m}, and C_{4m} fullereneynes respectively approach that of the previously proposed planar carbon phases 6,6,6-graphyne; 12,12,12-graphyne; and 18,18,18-graphyne (14.9, 23.7, and 26.3 kcal/mol carbon, respectively, based on group increments) [9], which are pictured in fig. 3. The increase in the (per carbon) formation energy of a C_n fullereneyne above the infinite molecule limit is expected to be smaller than the per carbon energy difference between a C_n fullerene and a graphite monolayer. Based on MNDO calculations on fullerenes, this energy is 4.7, 3.7 and 1.8 kcal/mol carbon for C_{180}, C_{240}, and C_{540}, respectively [12]. The limiting energy for the large C_{2m} fullereneynes (14.9 kcal/mol carbon) is close to the experimental value [13] for C_{60} in the gas phase (10.6 kcal/mol carbon). For the comparison, the proposed biphenylene-like cage compound called archimedene [14], which has a porous cage and I_h symmetry, has a heat of formation which is substantially higher than the calculated value [9,15] for the planar analogue of archimedene (19.6 kcal/mol carbon based on the measured heat of formation of biphenylene), which is pictured in fig. 3d.

Since C_{60} forms a face-centered cubic crystal struc-

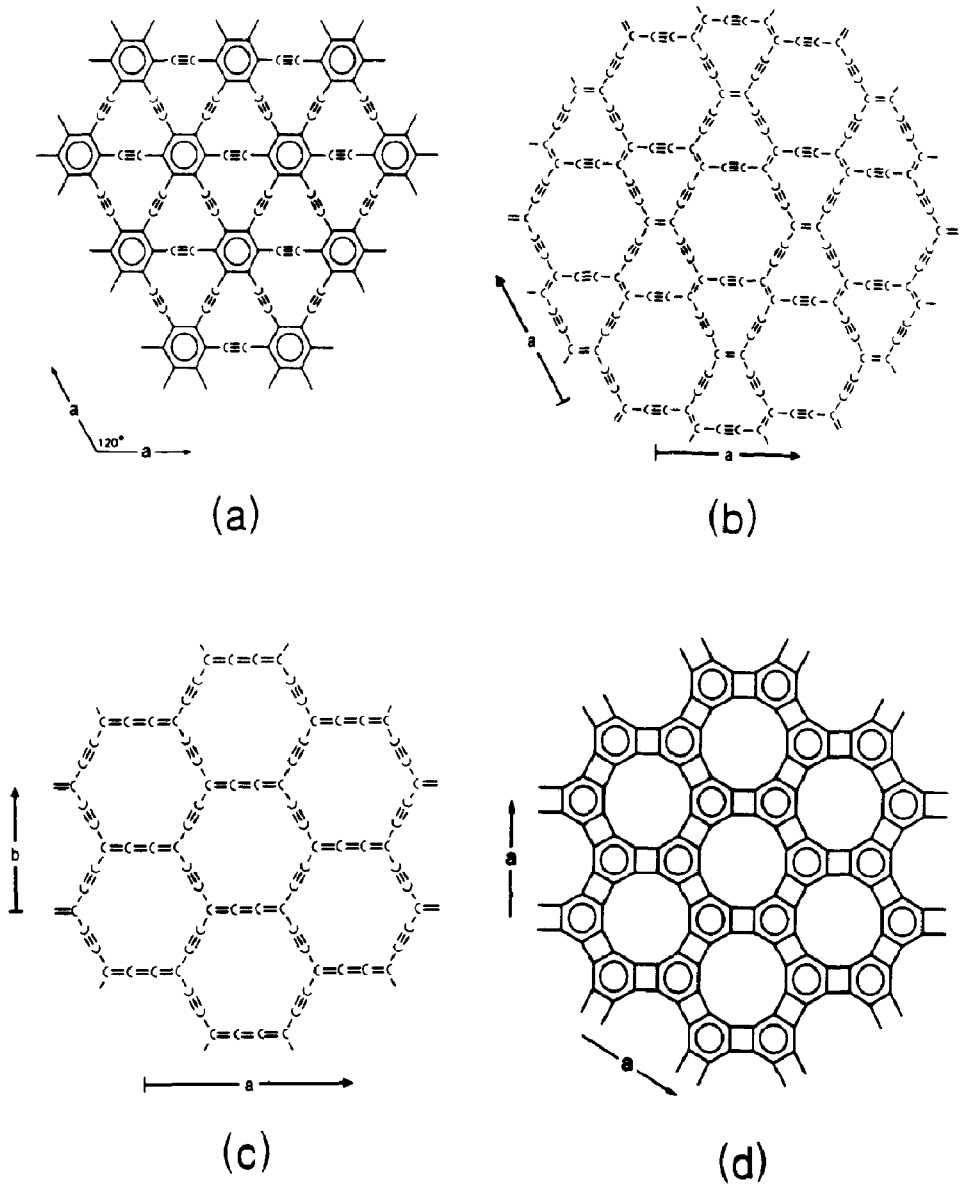

Fig. 3. Structures of proposed (a) 6,6,6-graphyne; (b) 12,12,12-graphyne; and (c) 18,18,18-graphyne carbon phases which correspond, respectively, to the infinite limits for the C_{2m}, C_{3m} and C_{4m} fullereneynes derived from a C_m fullerene. Part (b) shows the planar sheet analogue of archimedene. Hexagonal unit cell axes for (a), (b) and (d) and a possible orthorhombic unit cell axes for (c) are illustrated for the planar sheets.

ture, this close-packed structure (or a hexagonal close-packed structure having about the same energy) would be expected for the quasi-spherical fullereneynes. An estimate based on the calculated molecular radii and the van der Waals radius of carbon atoms ($R_{vdW}=1.7$ Å) yields the cubic lattice constants $a=20.7$ Å for the C_{120} solid and $a=25.5$ Å for the C_{180} solid. The corresponding densities are 1.09 g/cm^3 for the C_{120} solid and 0.87 g/cm^3 for the C_{180} solid. These values are significantly lower than that of the C_{60} fullerite, 1.65 g/cm^3 [1].

Note that the fullereneynes should form a variety

of types of novel charge-transfer and π-bonding complexes. For example, 1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-triyne contains the $(C(sp^2)$-$C(sp)C(sp)C(sp^2))_3$ rings found in both C_{120} and C_{180}. This hydrocarbon, which is pictured in fig. 4d, forms both Ni(0) and Cu(I) complexes, in which the metal is centered in the ring between the six C(sp) atoms [16]. Similar complex formation for C_{120} or C_{180} would provide fullereneyne balls in which one or more of the twenty ring cavities contain a metal atom or ion. The cyclic 1,5,9-tridehydro[12]annulene (fig. 4a), which also contains the same type of rings found in both C_{120} and C_{180}, forms both monoanions and dianions upon alkali-metal doping [1]. The same charge density per carbon as for the hydrocarbon dianion would provide a reduction level of up to 20 electrons for a C_{120} cage. Also relevant for complex formation, note that a face-centered cubic packing arrangement of fullereneyne molecules would provide one octahedral hole and two tetrahedral holes with large van der Waals radii (about 2.3 and 1.3 Å, respectively, for C_{120}, and 3.0 and 1.6 Å, respectively, for C_{180}), which could incorporate various dopant species. Consequently, the fullereneynes provide the possibility of reversible endohedral doping, cage-shell doping, and lattice interstitial doping.

Although the C_{120} and C_{180} fullereneynes will be very challenging to synthesize, they are not pathological structures. Stable molecules are well known that have quite similar ring structures to those found in the fullereneynes, such as (in fig. 4) compounds

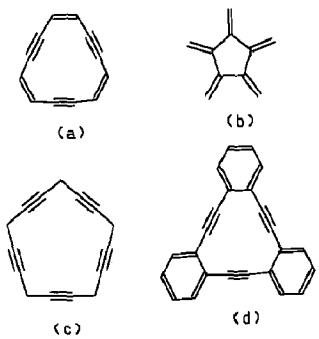

Fig. 4. Hydrocarbon molecules having similar rings as found in fullereneynes: (a) 1,5,9-tridehydro[12]annulene, (b) pentaradialene, (c) [5]pericyclyne, and (d) 1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-triyne.

(a) and (d) and derivatives of (b) and (c) in which the hydrogens are replaced by metals [16–19]. The open nature of the fullereneynes might be advantageous for relatively low temperature coupling of as few as three monomer units (containing combinations of such rings) to form either the C_{120} or C_{180} fullereneyne. The major effort required for a successful synthesis might be motivated by the novel porous structure of the fullereneynes, which provide predicted properties which are quite different from those of the well-known fullerenes.

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