On the geometry and conformation of starburst dendrimers

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In this work, we propose a geometrical model for the study of conformational properties of a starburst dendrimer with the topology of a truncated Bethe lattice. A convenient embedding of the Bethe lattice in the hyperbolic plane is used to study the architecture of the dendrimer. As results, we find an upper bound for the molecular size and the density profile.

1. Introduction

Recently, highly branched molecules called dendrimers or arborols have become increasingly important in macromolecular science [1,3,7,9,10,17,19,20]. Dendritic macromolecules are three-dimensional polymers that emanate from a central core, have a defined number of generations and functional end groups, and are synthesized in a stepwise way by a repetitive reaction sequence [20]. An important difference between linear polymers and dendrimers is that a linear polymer consists of an entanglement of single molecular chains. In a dendrimer, by contrast, the many branches give rise to a very high number of terminal functional groups in each molecule. In spite of their complexity, it is now possible to devise synthetic strategies which enable a systematic molecular morphogenesis from small molecules to macroscopic matter with control of size, shape, topology, flexibility and surface chemistry [20]. New synthetic paths can lead to materials with promising properties and potential new applications for catalysis, selective binding, electron transfer and energy conversion.

Dendrimers prepared from rigid units have a more precisely defined three-dimensional structure compared to their flexible counterparts. The rigid repeated units impose geometrical restrictions and thus little conformational freedom. Such freedom comes mainly from the rotational angles which depend on steric effects and/or hydrogen bonding [20]. The branching angle, on the other hand, is determined by the chemical nature of the branching juncture. A new, all-hydrocarbon, rigid macromole-

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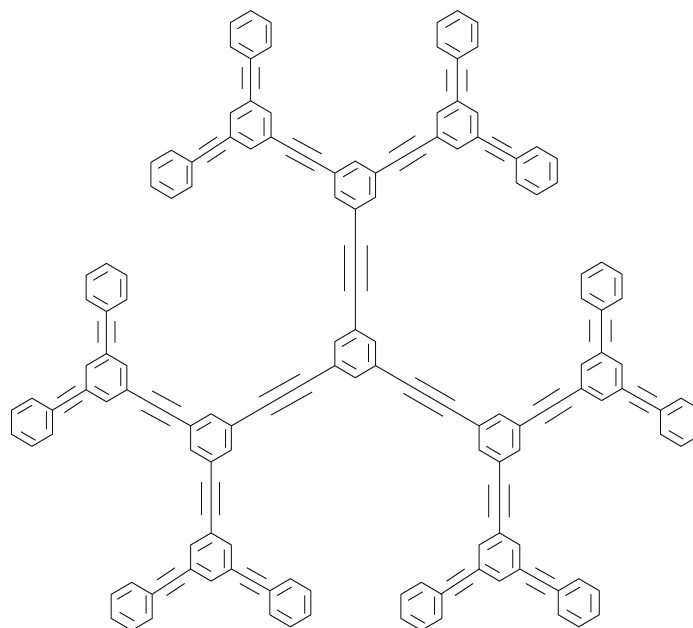
Figure 1. The core of the 94-mer phenylacetylene dendrimer.

cule, $C_{1134}H_{1146}$, has been recently synthesized and characterized [21], in spite of the steric strain which is quite dramatic in these dendritic systems [13]. This dendrimer consists of 94 phenylacetylene monomer units (94-mer in polymer speech). Its two-dimensional representation displays a snowflake-like skeleton (as shown in figure 1).

This 94-mer starburst dendrimer presents some outstanding geometrical properties. Its two-dimensional skeleton is isomorphous to the three-coordinated Bethe lattice [8]. Also, computer generated three-dimensional models exhibit a globular shaped surface with large voids and niches in its interior [21] reminiscent of a negatively curved surface. As we shall see, this implies that not only the topology of these molecules is that of the Bethe lattice, but also their geometry and symmetries. The conventional Bethe lattice is an infinite ramified network without rings and unable to fit entirely in the three-dimensional space since its number of vertices grows exponentially with the distance, while the available space grows only as a power law. Usually, it is viewed as a lattice in an infinite-dimensional Euclidean space. However, the Bethe lattice can be embedded in a constant negative-curvature surface, the Lobachevsky or hyperbolic plane [11,12,18]. There, it becomes a regular lattice with well defined bond angles and distances. Although a theorem due to Hilbert [6] forbids the entire hyperbolic plane to be isometrically immersed in the three-dimensional Euclidean space, a result of Cartan [2] permits a finite portion of the hyperbolic plane to do so. This appears as a wrinkled surface: the larger is the portion, the more crumpled it looks like. The maximum size would be that one beyond which the immersed surface begins to self-intersect, producing the geometrical analogue of steric strain.

In this article, we propose a hyperbolic dendritic model for the 94-mer starburst dendrimer in particular, but some of the results are general enough to apply to other rigid systems. The model enables us to study structural properties such as the dendrimer scaling behavior, its intramolecular density profile, and gives an upper bound for its molecular size.

2.   Hyperbolic model

The Bethe lattice has been widely used as a theoretical substrate for the modeling of many physical systems. It is defined as an infinite ramified set of points, each one connected to q neighbors, such that no closed rings exist, forming a completely open hierarchical structure. The natural hierarchy presented in such lattice provides the analytical treatment of a broad spectrum of theoretical problems, many of them analytically unsolvable when modeled in ordinary Euclidean lattices. On the other hand, behind those simple analytical solutions hide unusual geometrical characteristics [16]. By construction, the total number of vertices in the Bethe lattice grows exponentially with the distance. In this way, this lattice can be globally realized in an Euclidean space only if the space is of infinite dimension.

Perhaps a brief explanation is due here. One might try to build the lattice according to the following steps:

 (i) take a starting point on a given plane;

 (ii) draw three straight line segments of a given length from that point such that the angle between each neighboring pair is always 120 degrees;

(iii) at the end of each segment repeat step (ii) except that one needs not to redraw segments already existing;

(iv) go back to (iii).

It is fairly obvious that this leads to the honeycomb or hexagonal lattice (the crystalline structure of graphite). If one would like to avoid the rings, while keeping constant bond length and angles, very soon one would need to step out of the plane and keep building the lattice in three-dimensional space. Soon enough, the same kind of problem would be happening in three-dimensional space and one would need to step into the fourth dimension. And so on. Then, in order to build a Bethe lattice with an infinite number of vertices, and with equal bond lengths and angles, one would need an infinite-dimensional Euclidean space.

It is clear then, that when one tries to build the Bethe lattice on a flat surface, the result is something altogether different (honeycomb) or one would have to keep increasing the dimensionality of space while the lattice grows. Another alternative was pointed out by Mosseri and Sadoc [14]: if you allow for the surface to be curved in a certain way, then the lattice may be built to any desired extension. This curved surface has constant negative curvature and is known in the mathematical literature as
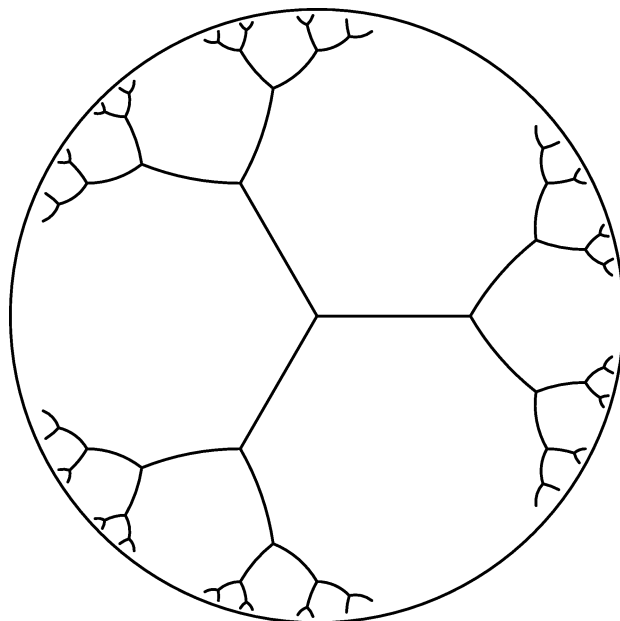
Figure 2. The trivalent hyperbolic Bethe lattice as represented in the Poincaré disc.

the two-dimensional hyperbolic space or hyperbolic plane [5]. Whereas a surface of constant positive curvature is a sphere, the corresponding constant negative curvature surface locally looks like a saddle. While the sphere has a finite area, the hyperbolic plane is infinite. Built on the surface of the hyperbolic plane, the Bethe lattice can be seen as a regular crystallographic lattice, presenting well defined angles between bonds and with spatial coordinates assigned to its vertices. In the hyperbolic plane, such a lattice is just a regular tiling of the "hyperbolic floor" by polygons of an infinite number of edges [14] just like the honeycomb is a tiling of the plane by hexagons.

Although the hyperbolic plane cannot be embedded in the three-dimensional Euclidean space, it can be presented as a projection onto a unit disc, the Poincaré disc. The points in the interior of the disc represent all the points of the hyperbolic plane, and the boundary of the disc represents the points at infinity. The geodesics are represented by arcs of circumference orthogonal to the boundary of the disc. The representation of the trivalent Bethe lattice in the Poincaré model can be seen in figure 2. The apparent distortion in the bond lengths, which are in fact all the same size, is due to the projection. More details on the geometry and symmetries of the hyperbolic Bethe lattice may be found in [11,12].

A hierarchical algorithm for constructing the Bethe lattice on the hyperbolic plane, yielding the coordinates of the vertices, has been described in detail in [12]. The computation of the distance between, say a given vertex and the origin involves geometrical concepts that do not properly fit in here, the interested reader may find the details in [11]. A word of caution: in statistical mechanics one usually deals with the topological distance, which is the number of bonds between two given sites of
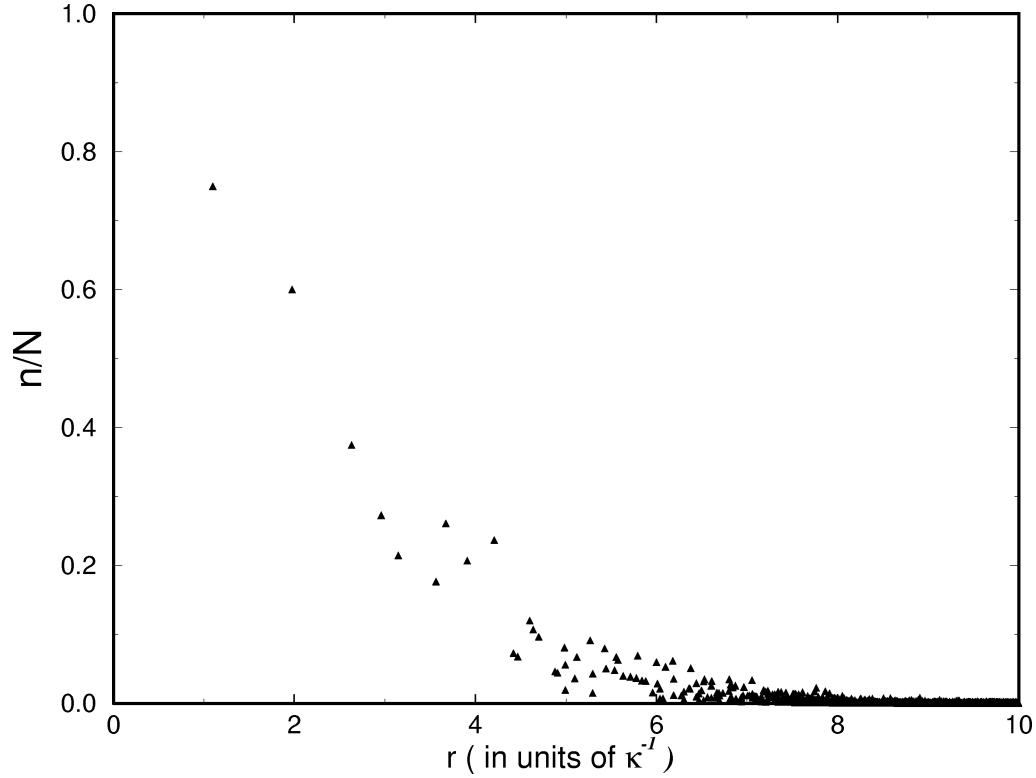
Figure 3. Rate between the number of surface vertices to the number of volume vertices n/N as function of the radial distance r.

the Bethe lattice. This is *not* what we do here. We use a physically more realistic distance: the actual geometrical distance as defined in hyperbolic space.

With the knowledge of spatial coordinates plus the possibility of defining geometrical distances between sites, one is able to analyze the scaling properties involving the way the number of volume (N) and surface (n) sites grow when the branched structure increases its size. For the purely topological q-coordinated Bethe lattice, it is well known that the total number of lattice points within a distance of t steps from the origin is

$$N = \left[q(q-1)^t - 2\right]/(q-2),\tag{1}$$

and the number of points at the lattice surface for the same distance t is

$$n = q(q-1)^{t-1}.\tag{2}$$

Therefore, for large t, the fraction n/N (surface/volume) is

$$\frac{n}{N} = \frac{q-2}{q-1}.\tag{3}$$

Thus, for a conventional Bethe lattice of any coordination number, the fraction n/N tends to a finite limit. This feature is quite different for finite dimensional Euclidean lattices, where the fraction n/N goes to zero in the thermodynamic limit. In the hyperbolic case we recover [16] the usual zero limit for n/N at large distances. This is shown in figure 3.

3.   Results and discussion

In this paper, the phenyacetylene dendrimer architecture is modeled by using a hyperbolic Bethe lattice that shares structural similarities to its two-dimensional structural formula. In this way, each one of the 94 benzene nuclei corresponds to a point in the three-coordinated Bethe lattice which is truncated after its fifth propagation. The nuclei are connected by rigid acetylene units. The 48 peripheral benzene nuclei are replaced by 3,5-di-tert-butylphenyl groups.

We base our model on the assumption that the equilibrium configuration of the dendrimer is that of minimum energy. Considering that the building blocks of the dendrimer are two-dimensional objects and that steric hindrance promotes an increase of the energy, the lowest energy requirement equals a maximum spread under the restriction of fixed branching angle and spacer length. In other words, the two-dimensional surface[1] defined by the dendrimer must be of maximal area and at the same time must permit fixed branching angles and spacer length. As seen in the previous section, the hyperbolic plane permits the growth of a structure isomorphous to the dendrimer and also with fixed bond angles and lengths, the Bethe lattice. Moreover, the area of a circle of radius r in the hyperbolic plane of Gaussian curvature $K = -\kappa^2$ is given by

$$A = 4\pi \sinh^2(\kappa r/2)/\kappa^2,$$

which is much larger than the area of an Euclidean circle of same radius, πr^2. That is, our model can be viewed as "variational" in the sense that the parameter κ is tuned to accommodate at the same time an area larger than the Euclidean one ($\kappa \neq 0$) and a commensurate three-coordinated Bethe lattice (from $\kappa d = \ln 3$, see below). In very simple words: if the dendrimer, being essentially a two-dimensional molecule due to obvious crowding reasons, cannot grow in the Euclidean plane, then it chooses a "roomier" two-dimensional space to do so.

The implication of figure 3 to our model is now evident: as the dendrimer grows, the distribution of benzene sites (or vertices of the Bethe lattice) over the volume of the molecule becomes much larger than the distribution on the external surface. This is a consequence of the crumpled nature of the Euclidean immersion of the hyperbolic plane and means that backfolding is taken into account in our model. In fact, this is obvious if one looks at table 1 of [11]. The immediate consequence for the phenylacetylene dendrimer is that 42 out of the 48, 3,5-di-tert-butylphenyl groups of the fifth generation, are on the surface while 6 of them lie within the spread of the previous generation.

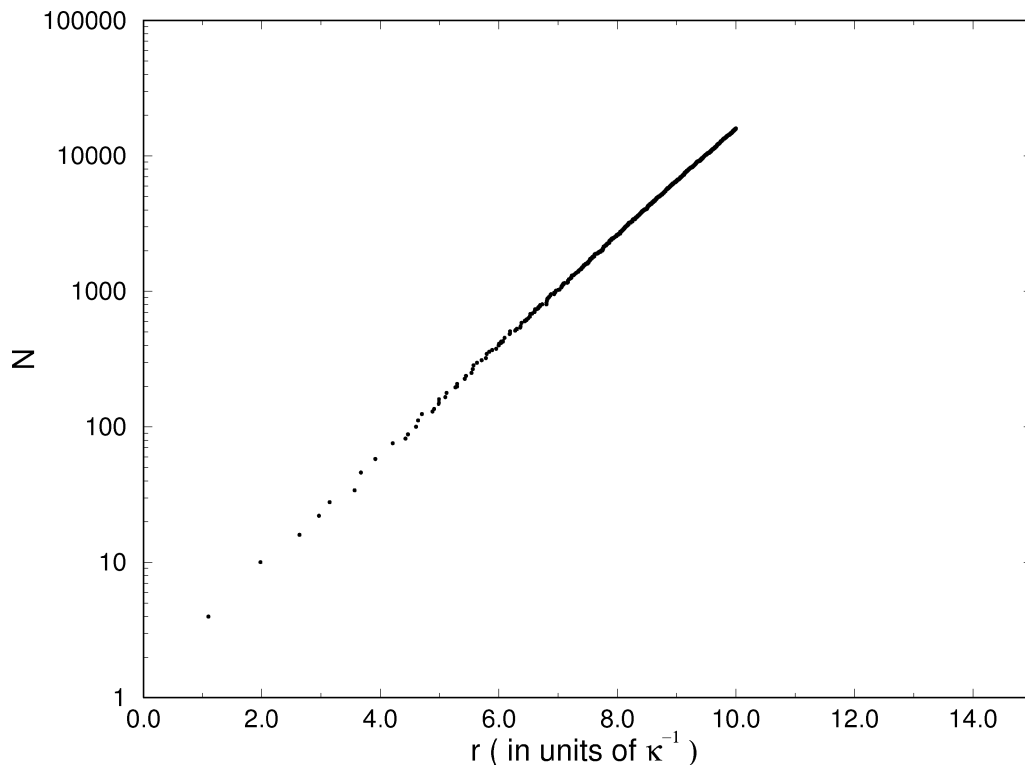[1] Not to be confused with the dendrimer outer surface.

Figure 4. Total number of vertices N within radius r, as a function of r.

In hyperbolic space, as on the surface of a sphere, the length scale is coupled to the radius of curvature, $R = 1/K$, of the surface. So, for example, if one wants to circumscribe a cube of edge length l, the radius of the circumscribing sphere has to be $l\sqrt{3}/2$ and one says that the cube and sphere are commensurate with each other. In our case, the Gaussian curvature of the hyperbolic plane commensurate with the three-coordinated Bethe lattice of edge (in this case the distance between two adjacent vertices) d, is given by the relation $\kappa d = \ln 3$ from [12]. Now, d is the length of the phenylacetylene unit which is estimated to be 7.0 Å. With this value, the constant κ is 0.157 Å^{-1} and the curvature K is -0.025 Å^{-2}. The hyperbolic model also provides an upper bound for the molecular size by considering the phenylacetylene dendrimer isomorphous to the fifth propagation of a negatively-curved three-coordinated Bethe lattice. Figure 4 depicts the total number of vertices N within a radius r from the core, as a function of r, for the hyperbolic Bethe lattice [16]. For the 94-mer phenylacetylene dendrimer ($N = 94$), one obtains from that plot that r equals 4.60 (in units of κ^{-1}) which gives an upper bound radius of 29.3 Å for the molecule. This is in good agreement with the value 27.5 Å estimated from space-filling molecular models [21].

It is expected that, as the volume of a dendrimeric molecule increases cubically, its mass increases exponentially [3,20]. As shown in figure 4, the total number of vertices
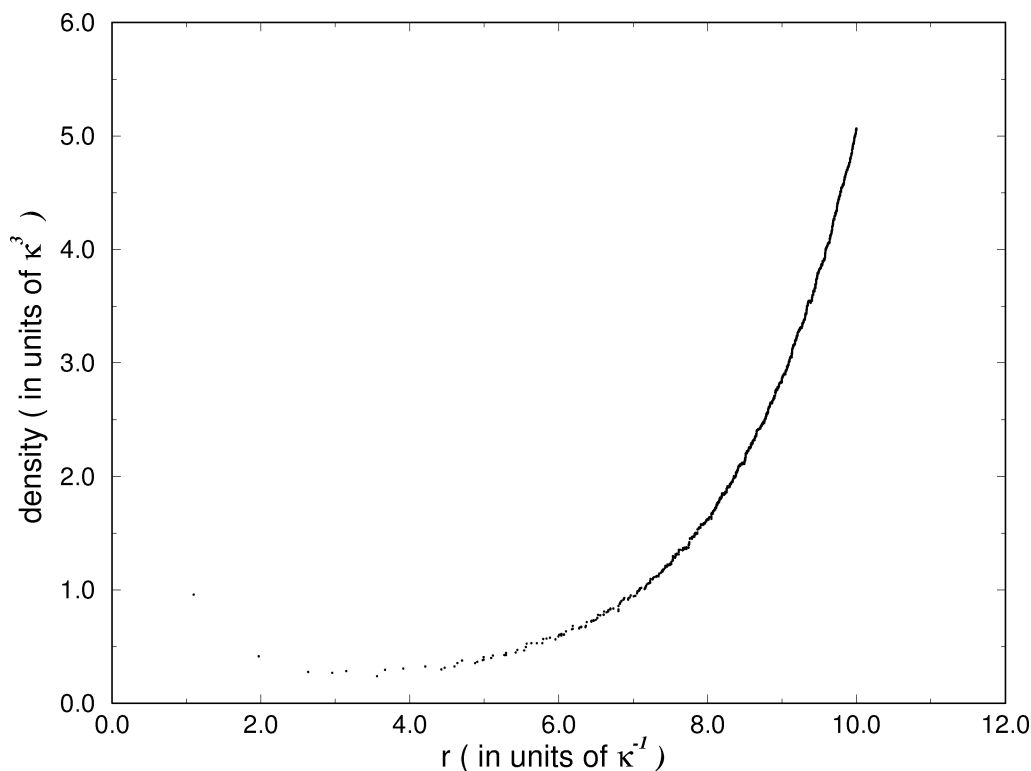
Figure 5. Density profile for the hyperbolic model.

(or molecular mass in suitable units) in our model also increases exponentially with its metric distance to the core. Figure 5 shows the density profile obtained from figure 4 by dividing $N(r)$ by the volume of a sphere of radius r. It shows an initial decrease, goes through a minimum and from then on keeps increasing with the radius.

In contrast to molecular models [15] that are able to predict the molecular weight threshold corresponding to the transition from an extended to a globular shape, our model concentrates in the globular shape side of the transition. Moreover, in order to have its maximum conformational freedom, a necessary condition to reach the minimum energy, the dendrimer is assumed to be in solution. The conformation of dendritic macromolecules in the solid state and in solution is still controversial [3]. Lescanec and Muthukumar [9] developed a model which predicts inward folding of branch units, a density profile maximum at the core of the dendrimers, and a distribution of terminal groups throughout the structure. This model simulates kinetic growth of a starburst dendrimer by means of a self-avoiding walk algorithm. Klushin and Mansfield [10] developed versions of the self-avoiding model to study polyether dendrimers in equilibrium through Monte Carlo simulations. Their model presents a dispersion of end groups throughout the molecule, even near the core, something that substantially lowers the density even considering backfolding. As a result, their density profiles decrease

with the size of the molecule. De Gennes and Hevert [4] developed a self-consistent field model which predicts a dendrimer structure emanating radially outward with a density profile minimum at the center of the dendrimer. In their model, all the terminal groups are on the periphery of the macromolecule and the ideal dendritic growth will only occur until a certain generation is reached at which point steric congestion will prevent further growth. Molecular modeling performed by Goddard et al. [15,20] predicts internal cavities, most of the terminal groups on the surface of large dendrimers and an increasing density profile. The density profile (figure 5) obtained in this letter, quite surprisingly, shows characteristics of all the above models! Initially it decreases with the radius, then it picks up and keeps increasing with the radial distance from the core. This is certainly a good indication of the important role of geometrical aspects in dendrimer modeling. Of course it would be a very naïve assumption to think that geometry alone solves the problem. On the contrary, we believe our contribution indicates that there is something in between molecular modeling/self-consistent modeling and kinetic/Monte Carlo models and perhaps the liaison is geometry.

In this work, a hyperbolic-geometrical model has been used to investigate starburst dendrimer architecture. Although we have focused our work on the phenylacetylene dendrimer, most of the results are general enough to be applied to other rigid dendrimers.

Acknowledgements

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