

# Modeling and Mass–Distance Scaling of a Nanometer Starburst Polymer

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## ABSTRACT

We report numerical scaling of cumulative mass with intramolecular distance of a model of one of the four segments of the hyperbranched poly(propylene-imine)-*dendr*-DAB(CN)<sub>64</sub> molecule. Assuming prevalent repulsive link–link forces gives a power law relation with non-Euclidian exponent  $d = 2.12 \pm 0.10$ , in close agreement with the known exact value  $d = 2$  of the universality class of isolated branched polymers with negligible loops. This outcome implies that the dendrimer molecule DAB(CN)<sub>64</sub> under good solvent conditions can be considered a mass fractal (non-compact structural pattern) with considerable open spacing, causing delayed diffusion of trapped species and a range of fracton modes in its low-frequency spectra.

**Keywords:** Simulation, dendrimer, mass–distance scaling, mass fractal, delayed diffusion.

## INTRODUCTION

The branched nanostructures of high-stage dendrimer molecules have shown their usefulness and applications for controlled drug release, host–guest chemistry, catalysis, and optical phenomena [1–4]. Evidently, some of these properties must be based on a dendrimer’s structural spatial pattern to furnish, in addition to its interior “dendritic box”, sufficient openings for the trapping of smaller molecules. The question then comes to mind whether, in general, such a dendrimer could approximate a mass fractal with delayed interior transport and, in particular, the value of its fractal dimension and range of the linear scaling variable [5].

Recently, results from small-angle neutron scattering (SANS), viscosity, and molecular dynamics calculations on five stages of diaminobutyl poly(propylene-imine) species DAB(CN)<sub>X</sub> and DAB(NH<sub>2</sub>)<sub>X</sub>, with  $4 \leq X \leq 64$ , have been applied to scale radius of gyration ( $R_G$ ) with molecular mass ( $M_G$ ),  $R_G \sim M_G^{1/d}$ , leading to  $d \approx 3$  and thus implying compact (space-filling) structures [6]. However, inspection of the  $R_G$  vs  $M_G$  plots generated from the data [7] shows a definite, monotonously convex non-linearity of the log–log functionality of these scaling operations. In addition, there is no verification offered [6] on a tacit assumption that the species are mutually self-similar [8, 9]; it seems unlikely that a low-molecular stage, say DAB(CN)<sub>8</sub> of molecular weight 741, and a polymer such as DAB(CN)<sub>64</sub> (mw 6910), have mutually self-similar mass distributions and even if

the self-similarity condition were satisfied among the higher synthetic stages  $X = 16, 32, 64$ , the scaling range of  $M_G$  would then cover the insufficient factor of 4 to 5 [5].

It is thus appropriate to explore whether dendrimers are close approximations of a mass fractal by using some less complex, more transparent and direct method, namely, by performing mass ( $M$ ) – distance ( $R$ ) scaling simulations on the presently highest-stage species DAB(CN)<sub>X</sub>,  $X = 64$ , where  $R$  now is a distance parameter of physical range  $r \leq R \leq R_G$  within the molecule — quantity  $r$  and radius of gyration  $R_G$  furnishing its lower and upper cutoffs [10, 11],

$$M \sim R^d. \quad (1)$$

The resulting value of  $d$  can then be compared with the exact result ( $d = 2$ ) for a large, branched, isolated polymer (with only minor contributions of looping structures) under prevalent repulsive interlink forces (good solvent) [12].

Exploitation of Eq.1 requires the generation of a complete set of atomic coordinates of the dendrimer based on structural information, its schematic layout being displayed below in Fig. 1. Yet the generality of a fractal approach is such that a fractal dimension is not indicative

Structural Layout of a DAB(CN)<sub>64</sub> Segment

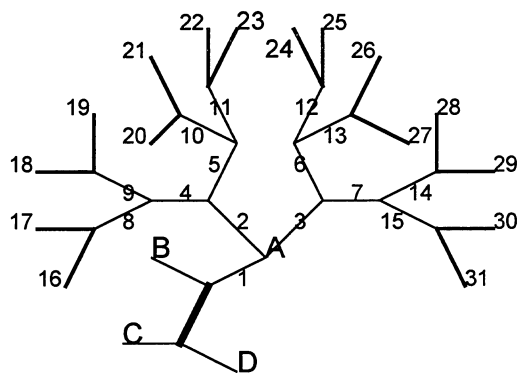


Figure 1. The thin number-identified lines represent the 15 propyl-N< links, the thick lines show the 16 end-standing ethyl-CN groups numbered at their end. The thick line is the butyl group of the diaminobutyl core, with the locations of segments B, C, and D indicated.

of a given set of specific bond lengths and angles but only of the structural pattern of the object, meaning that an *equilibrium* configuration need not be known. Since the terminating  $-(\text{CH}_2)_2-\text{C}\equiv\text{N}$  groups have nearly equal mass distribution as the  $-(\text{CH}_2)_3-\text{N}<$  links, effects from the position of the end groups — still a controversial subject [4, 6] — on the analysis can be minimized if the mass count is repeated from several points within the molecule. Finally, it suffices to consider only one of the four near-equal segments of the dendrimer molecule, a segment being made up of fifteen  $-(\text{CH}_2)_3-\text{N}<$  and sixteen  $-(\text{CH}_2)_2-\text{C}\equiv\text{N}$  groups [1, 13].

To proceed, a large, three-dimensional mechanical model with realistic relations among bond distances, atomic size, angles of atomic orbitals, and non-bonded atom-atom separations was constructed on a useful, workable, relative scale. From its resulting  $x, y, z$  atomic coordinates, the measure of incremental atomic mass points falling within distance interval  $\Delta R$  at distance  $R$  was taken, with  $\Delta R$  corresponding to the average covalent (C, N) and van der Waals diameters (H), respectively, and  $R$  counted off a chosen origin within the molecule. Subsequently, a plot of the (common) logarithm of cumulative mass  $\Sigma M$  vs the logarithm of distance  $R$  was generated (Eq. 1) and the linear portion of its slope identified with mass-distance scaling dimension  $d$  of the molecule.

## MODEL AND COORDINATE SYSTEM

**Model.** A molecular segment [1, 13] of  $\text{DAB}(\text{CN})_{64}$  was constructed from model set MINIT [14]. The structure was affixed to a base plate overlaid by a graduated horizontal  $27 \text{ cm} \times 18 \text{ cm}$  grid, indicating the object's size.

**Coordinate System.** The  $x, y, z$  coordinates of each of the 93 C, 15  $-\text{N}<$ , 16  $\equiv\text{N}$ , and 154 H atoms were read off at the touching point of a calibrated plummet line with the  $x, y$  grid and verified using Sigma Plot 5.0™. The C-H and C $\equiv$ N distances were fine-tuned to correspond, relatively, to 1.090 and 1.150 Å, respectively [15]. Adjustment of the sets of the three N-C distances off the fifteen branching

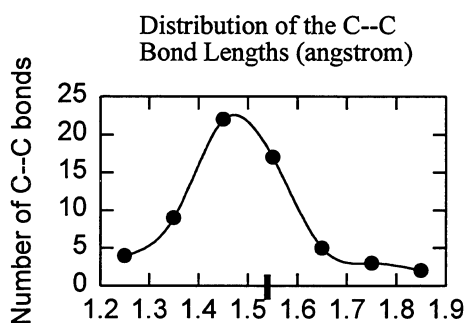


Figure 2. C-C variations from the norm.

N atoms to its accepted value of 1.469 Å [16] was also performed if necessary, but the C-C bond lengths, angles of the  $sp^3$ -orbitals, and variations of the C-N-C angles from  $120^\circ$  were left as is because the accruing coordinate shifts iterated to unacceptably large error levels. The resulting distribution of the C-C distances (accepted value 1.54 Å), shown by Fig. 2 (at bottom in the left column), and the distribution of the C-N-C angles (70% between  $108$  and  $118^\circ$ ) is deemed acceptable within our approach.

## RESULTS AND DISCUSSION

**The Virtual Molecule.** Figure 3 displays a rendering of the segment's branching pattern by the Molecular Visualization Program *RasMol* [17] (version 2.6) on the basis of the set of  $x, y, z$  coordinates of the 278 atoms, connectivity of their 277 bonds, and covalent or van der Waals diameters as described in the previous section. The color coding of the atoms is explained in the caption. The

Representation  
by *RasMol* of one Segment of  
 $\text{DAB}(\text{CN})_{64}$

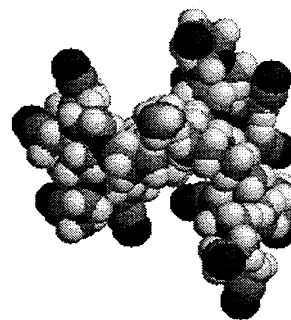


Figure 3. Color code: The C atoms are light gray, the branching N atoms are black, the end-standing N atoms are dark gray, and the H atoms are white.

shape of the structure is quite non-spherical, serrated, but keep in mind that the diaminobutyl core of the full  $\text{DAB}(\text{CN})_{64}$  molecule carries three additional and near-identically shaped patterns of this segment [1, 13] (Fig. 1).

Finally, using *RasMol*'s visual and numerical tests on bond lengths, orbital and dihedral angles as well as atom to atom distances, seven instances of an abnormality (non-bonded H-H separations below 1 Å) were detected but considered insignificant (see APPENDIX).

**Mass Distance Scaling (Eq. 1).** Distances  $R = (x^2 + y^2 + z^2)^{1/2}$  were sorted by magnitude and divided into equal size intervals  $\Delta_1 = \{0 \leq R_1 \leq 1\}, \dots, \Delta_{13} = \{12 \leq R_{13} \leq 13\}$ , hence  $\Delta_k$  equaling about Pauling's covalent or van der Waals atomic diameters [18]. Incremental mass count  $M_n$  of atomic species  $n$  was grouped within its appropriate  $\Delta_k$  and

distance  $R$  taken as the average value of all  $R_k$  ending within  $\Delta_k$  [19] and counted from the center of mass.

The resulting  $\log \sum_n M_n - \log R$  plot (Eq. 1) is displayed by Fig. 4 (●) below, with linear least-squares slope  $d = 2.12 \pm 0.10$  (standard deviation).

The entire scaling procedure was then reapplied with  $R\{0,0,0\}$  chosen (i) at the C atom which bonds the segment to one of the N atoms of the diaminobutyl core (▲) and (ii) at one of the outermost -N< atoms (○, slope not drawn), respectively. Note that the decrease of the slope at highest  $R$  arises naturally as the sweeps of the radius vectors add few mass points near the rims, whereas data fluctuations about the line at the smallest  $R$  values are caused by low

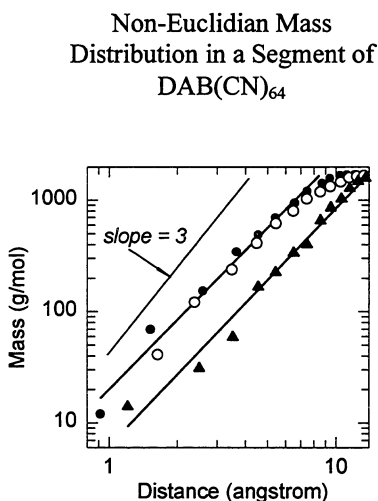


Figure 4. Mass-distance scaling of a dendrimer segment. The slope of a compact pattern is indicated.

mass counts close to the chosen origins. The equality of the slopes show that effects from the  $-(\text{CH}_2)_2-\text{C}\equiv\text{N}$  end group locations are effectively averaged out.

**Fractal Aspects.** The resulting mass-distance scaling dimension  $d = 2.12$  is good over a linear scaling range of  $R$  covering a factor of about eight, interspersed within the physically realistic intramolecular lower and upper cutoffs, namely, covalent atom diameter  $r$  (1.4 Å) [18] and radius of gyration  $R_G$  (14 Å) [6], respectively.

Second, mass fractal dimension  $d = 2.12$  agrees well with the exact value  $d = 2$  for the large, branched polymer: The simulated value of the mass-distance scaling dimension of the branching pattern of stage  $\text{DAB}(\text{CN})_{64}$  is close to the exact value of the mass-distance scaling dimension of the *limit* — the fractal ( $X \rightarrow \infty$ ) — of the system's pattern within the stated condition of solvent quality [12, 20].

## CONCLUSIONS AND PREDICTIONS

We have shown, on hand of a simulation of a straight mass-with-distance scaling operation on a realistic model,

that dendrimer species  $\text{DAB}(\text{CN})_{64}$  can be considered a very good approximation of a mass fractal of mass fractal dimension  $d \sim 2$  within embedding space dimension  $E = 3$ . Hence, the structural pattern of the  $\text{DAB}(\text{CN})_{64}$  molecule under the chosen boundary condition (good solvent) must contain considerable open space, but its “where” and “how” are questions outside the applied analysis.

Considering the  $\text{CH}_2$  groups as points of mass 14 yielded  $d = 2.07 \pm 0.06$  (plot not shown), proving that the detailed analysis is free of serious errors.

The results infer that there is much more to the structural pattern of this molecule than would follow from the usual Euclidian assumptions [6]. For instance, diffusion within the dendrimer would be anomalous (delayed) and low-frequency spectral data are expected to contain a region of fracton modes [12, 21].

Furthermore, not only prevalent solvent conditions but also temperature effects can be expected to alter the specifics of the density distribution of the system's branching pattern, such as its increasing degree of collapse ( $d \rightarrow 3$ ) under increasing temperatures, as manifested by the concomitant decrease of the fracton range [22].

## ACKNOWLEDGMENT

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## APPENDIX: LINK SEPARATIONS

From the data set of the  $x, y, z$  coordinates of the segment's structure one readily obtains a quantitative indication on the separation between the various links, their positions outlined in Fig. 1. Such an estimate, quite useful in order to verify that the simulated branching pattern corresponds indeed to the stated boundary condition of prevalent link-link repulsive forces, is most appropriately based on the non-bonded hydrogen-hydrogen distances.

To proceed, we computed all non-bonded intra- and interlink H-H distances under the reasonable upper cutoff of 5 Å and labeled them by the all the pairs of intervening H atoms within any two given pairs of interacting links. The links themselves were identified by the difference of their link numbers (refer to Fig.1 in the text). For instance, the separation number ‘0’ designates the number average of all such H-H separations that are of distances below 5 Å and relevant to *intra*link non-bonded H atoms, whereas the separation numbers  $n \geq 1$  refer to all the number-averaged *inter*link distances falling below 5 Å; in other words, the H-H interactions between different links.

The total link separation count, respecting the chosen upper cutoff, then refers to link numbers  $L$  and  $L + n$  with  $0 \leq n \leq 25$  and  $1 \leq L \leq 31$ . For example, the non-bonded H-H interactions which originate from the six H atoms on link 1 contribute (i) 12 intralink distance terms within link 1 and (ii) 20, 28, 25, 12, 8, 9, 2, 5, 1 interlink terms between link

1 and links 2, 3, 4, 5, 6, 8, 9, 10, 19, respectively, all below upper cutoff distance 5 Å.

The overall result for the entire system is displayed by Fig. 5 below. From the plot it is apparent that the vast majority of all non-bonded interhydrogen separations have magnitudes that fall between 3 and 4 Å. Seven short H-H separations, of magnitudes between 0.366 and 0.964 Å, are isolated events not involving multiple H-H interactions between links.

Hence the overall structural pattern, displayed by Fig. 3 in the text, indeed simulates essentially repulsive interlink forces (good solvent quality) as demanded by the boundary condition.

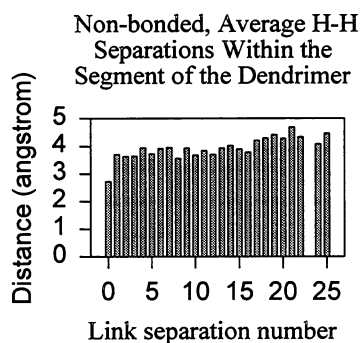


Figure 5. Non-bonded interhydrogen distances below a cutoff of 5 angstrom and labeled by the difference of the link numbers as indicated in Fig. 1 of the text.

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- [14] ©Cochranes of Oxford molecular models, Wiley-VCH: Weinheim, 1978. For instance, C-C model distance 1.500 cm is translated by *RasMol* as 1.500 Å.
- [15] Distances computed from the pdb-files of  $C_{19}H_{40}$ , (5S,9S)-5,9-dimethylheptadecane, ©1998 D. Woodcock, Okanagan University College, Kelowna, B.C., Canada. <http://www.sci.ouc.bc.ca/chem/molecule/molecule.html>.
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