

structure D, which was substantiated by an LSPD₂ experiment; irradiation of the H-16 proton at δ 7.44 collapsed the C-18 (dd) signal into a doublet ($J = 8$ Hz). It was concluded that C-27 in C was linked to C-28 in D, which was supported by a 1-Hz allylic coupling between H-27 and H-29. This was also evidenced by an LSPD experiment; irradiation at δ 4.78 affected the C-28 and the C-29 signals. Then the C-12 oxygen moiety in B can be linked to the C-19 carbonyl group in C to make an ester linkage. This was also shown by an LSPD experiment; irradiation at δ 5.29 changed the shape of the signal at δ 171.6. The last group to be assigned possessed a composition of CH₂NO including a ¹³C NMR signal at δ 157.3 and a ¹H NMR signal at δ 6.48 (2 H, br s, exchangeable). These features are characteristic of a carbamate group. A ³J_{C-H} (3 Hz) observed between H-21 and the carbamate carbon led us to place the carbamate group at C-25. The configuration of the 13 chiral centers remains to be elucidated.

Kabiramide C possesses an unprecedented three contiguous oxazole ring system, which might be biosynthesized by a cyclization of a triserine moiety. Nudibranch eggmasses from Kabira Bay contained considerable amounts of kabiramide C (0.03% of wet weight), whose roles and origin, whether it is produced by the nudibranch or derived from a food source, are interesting subjects.

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Supplementary Material Available: ¹H NMR, ¹³C NMR, (¹H, ¹H) COSY, and (¹H, ¹³C) COSY spectra (4 pages). Ordering information is given on any current masthead page.

Cascade Molecules:¹ Synthesis and Characterization of a Benzene[9]³-Arborol

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The synthetic aspects of a novel class of cascade molecules called arborols have recently been described.¹ Tomalia et al.³ have recently reported a similar class of cascades called "Starburst-Dendritic" polymers. Our initial unidirectional cascade design, derived from the Leeuwenberg model for trees,⁴ generated a unique spherical hydrophilic surface covering a compact lipophilic core. Application of the synthetic techniques to a three-directional model (Figure 1) has led to the herein described benzene[9]³-arborol (**1**), in which the three cascade spheres are attached to a central benzene seed. Further, with increasing spherical volume it should be possible to visualize a triad using electron microscopy, thus affording direct substantiation of the arborol concept.

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Figure 1.

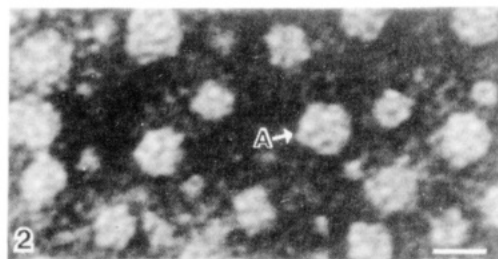


Figure 2. Transmission electron micrograph of **1**, negatively stained with 2% phosphotungstic acid. Note aggregation of **1** into micelles of ca. 200-Å diameter. Bar = 200 Å; 390000× magnification; 80-KV accelerating voltage.

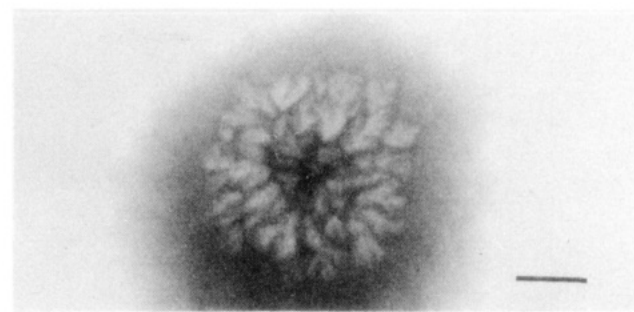


Figure 3. Microcrystalline region of transmission electron micrograph of **1**. Bar = 100 nm; 100000× magnification.

The synthesis of **1** (Scheme I) proceeded by selective free radical bromination⁵ of mesitylene with *N*-bromosuccinimide in CCl₄ to give (30%) 1,3,5-tris(bromomethyl)benzene (**2**), which upon treatment with 3 equiv of NaC(CO₂Et)₃⁶ afforded (88%) the nonaester **3** [oil; ¹H NMR δ 1.21 (t, CH₂CH₃, $J = 7.2$, 27 H), 3.41 (s, ArCH₂, 6 H), 4.20 (q, CH₂CH₃, $J = 7.2$ Hz, 18 H), 7.02 (s, Ar H, 3 H); ¹³C NMR δ 38.4 (ArCH₂), 66.6 (CH₂C), 166.4 (CO);⁷ IR (neat) 1746 (C=O) cm⁻¹]. The second tier, which incorporates the polar functional groups, was introduced by amide formation; thus, treatment of **3** with tris(hydroxymethyl)amino-methane at 70 °C in Me₂SO gave (40%) the benzene[9]³-arborol (**1**) [mp 135–140 °C; ¹³C NMR (D₂O) δ 64.0 (HN⁴C), 64.4 (ArCH₂C), 174.6 (CO); IR 1682 (C=O) cm⁻¹]. Even with a mass of 1485, this arborol is highly water-soluble.

For complete characterization, **1** was converted into its benzoate derivative by treatment with benzoyl chloride⁸ to afford (90%) the tris(nonabenzoate) **4** [mp 88–90 °C; ¹³C NMR δ 166.2 (CONH), 162.8 (CO), 133.6 (C4), 129.8 & 128.6 (C2 and C3), 127.2 (C1); IR 1725 (ester), 1680 (amide) cm⁻¹]. The NMR (¹H and ¹³C) spectra of ester **4** exhibited considerable line broadening in the aromatic region, which is attributed to the expected steric overcrowding.⁹ Ester **4** is highly soluble in most organic solvents (CHCl₃, C₆H₆, CH₃COCH₃) and completely insoluble in water; it is, however, very hygroscopic!

In order to provide insight into the mode and size of aggregation, arborol **1** (0.7 mmol solution) was negatively stained, air dried, and examined by transmission electron microscopy; a representative micrograph is shown in Figure 2, where aggregates¹⁰

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Scheme 1

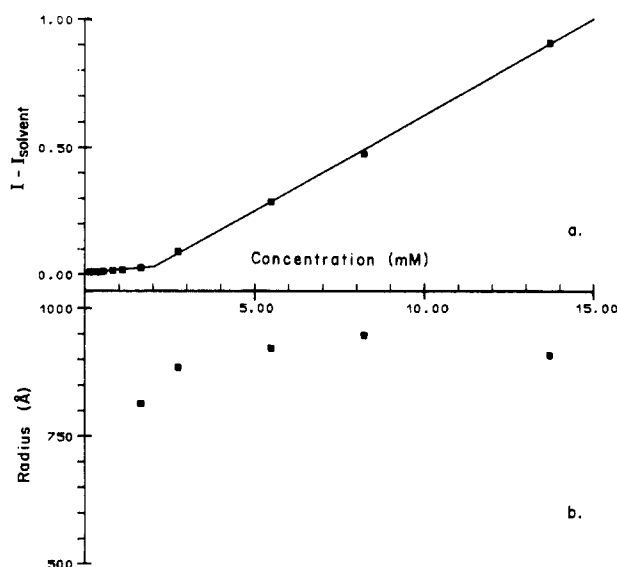
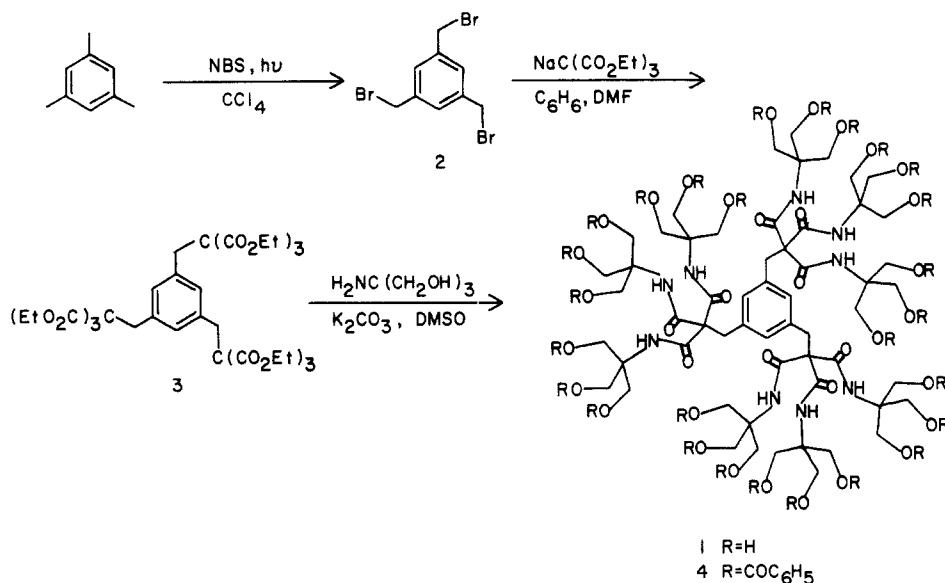


Figure 4. (a) Concentration dependence of the intensity of scattered light (scattering angle $\theta = 90^\circ$). The lines shown use the result of a least-squares fit with $m = 6175$, $b = 8478$, and $r^2 = 0.967$ and $m = 40656$, $b = -61017$, and $r^2 = 0.999$ for the data from 0.137 to 1.64 mM and from 2.74 to 13.7 mM, respectively (cmc = 2.02 mM). (b) Concentration dependence of the calculated Stokes radius. Values below 1.0 mM showed signs of an insufficient number of particles in the sample volume and have been omitted.

of **1** appear as light areas (~ 200 -Å diameter) against a darker background. Close examination of Figure 2 reveals the triangular arrangement of cascade spheres visible on the surface of the aggregate. Calculations using dimensions determined from molecular models indicate ca. 40 molecules of arborol **1** per aggregate (Figure 2, e.g., aggregate A). Figure 3 shows a TEM of a higher concentration region where microcrystals of arborol **1** have formed.

The micellar character of aggregates of **1** was also evaluated by light scattering experiments. The intensity of scattered light ($\theta = 90^\circ$), as a function of concentration, is shown in Figure 4a. The change in scattered intensity at a concentration of 2.02 mM is indicative of the critical micelle concentration (cmc). Dynamic light scattering gives a Stokes radius for the aggregate of ca. 950 Å (Figure 4b) and shows only minor dependence on concentration above CMC.

Development and exploitation of these new polymeric cascades are in progress.

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Supplementary Material Available: Experimental, electron microscopy, and light-scattering details (3 pages). Ordering information is given on a current masthead page.

Preparation of a Novel Sulfur-Nitrogen Cage Compound by the Transamination of Bis(dimethylamino) Sulfide with a Macrocyclic Tetrakis(secondary amine)

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Transamination of tris(dimethylamino)phosphine with the macrocyclic tetrakis(secondary amine) 1,4,7,10-tetraazacyclododecane ("cyclen") results in oxidative addition of one of the N-H bonds to the trivalent phosphorus atom to give the pentavalent phosphorus-hydrogen compound $C_8H_{16}N_4PH^{1,2}$ which is an important synthetic entry to other phosphorus(V) derivatives exhibiting novel structural features.^{3,4} This paper reports the transamination of bis(dimethylamino) sulfide with the same macrocyclic tetrakis(secondary amine). This reaction not only proceeds totally differently from the corresponding reaction of tris(dimethylamino)phosphine but gives an unexpected and unprecedented type of sulfur-nitrogen cage compound.

In a typical experiment 5.0 g (29 mmol) of 1,4,7,10-tetraazacyclododecane⁵ is boiled under reflux in 35 mL of bis(di-

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(10) The initial concentration of **1** was below the cmc; however, aggregation occurred upon concentration during drying.