

Table I. Pseudo-First-Order Rate Constants for the Catalyzed Cyclization of 0.19 mM Compound **1** in 10% v/v DMSO in Water with 10 mM HEPES^a Buffer, pH 7.0, 37 °C

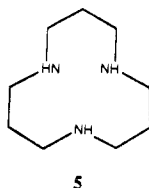
catalyst ^b	k_c , 10 ² h ⁻¹	k_{rel}
4	0.074 ± 0.001	1.0
2	0.690 ± 0.006	9
3	1.50 ± 0.01	20
Zn ²⁺ + Im	1.68 ± 0.02	23
Zn ²⁺ ^d	1.71 ± 0.12	23
Zn ²⁺ · 5 complex ^d	4.64 ± 0.27	63

^a4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid. ^bAll at 0.5 mM. ^cCorrected for the small background rate at this pH. ^dIn H₂O solvent without DMSO.

For this series we use the Zn²⁺ complex of the macrocycle **4** that was first examined by Rich and Stucky³ and further studied by Woolley.⁴ We have also described the catalysis of some phosphate ester hydrolyses by **4** and various of its derivatives.⁵ These are easily prepared by reaction of a 2,6-diacetylpyridine with dipropylenetriamine and Zn²⁺ salts, if one of the acyl groups is small so the first condensation reaction is relatively unhindered.

For the synthesis of **2**, lithium thiophenoxide was orthometalated with *tert*-butyllithium, and 1 equiv of this anion was then added to pyridine-2,6-bis(dimethylcarboxamide), followed by 1 equiv of MeLi. The resulting 2-acetyl-6-(*o*-mercaptobenzoyl)pyridine was treated with dipropylenetriamine and ZnBr₂ in the standard manner³⁻⁵ to afford **2** as an orange solid, mp 255 °C dec.⁷ For the synthesis of **3**, the above intermediate mercapto diketone reacted with 2-fluoroimidazole to attach the imidazole group to the thio, and with the dipropylenetriamine reaction this diketone,⁶ mp 186–188 °C, afforded **3** as a light yellow solid, mp 135 °C dec.

We have examined the rate of the reaction of eq 2 with these catalysts and with various other comparison systems. The data are listed in Table I. Uncomplexed Zn²⁺ is more effective than is the deactivated Zn²⁺ in **4**; interestingly, a Zn²⁺ complex of 1,5,9-triazacyclododecane (**5**) is better than zinc alone.



The addition of thiophenol or imidazole catalytic groups, in compounds **2** and **3**, increases the effectiveness of **4** by 9- and 20-fold, respectively. Both **2** and **3** show bell-shaped pH vs rate profiles, with rate maxima near pH 9.0, as expected for the bifunctional mechanism.

Bifunctional catalysts can be based on structure **5**, whose zinc complex is not deactivated. An additional binding group can be added, as we have done with **4**.^{5b} Unnecessary flexibility can be removed, although we have shown that some flexibility must be

left in catalyst systems so they can accommodate to the changing geometry of the reaction path.⁸ With such improvements we can hope for even better mimics of the zinc-base bifunctional catalysis used by many enzymes.

Acknowledgment. This work was supported by the U.S. Office of Naval Research.

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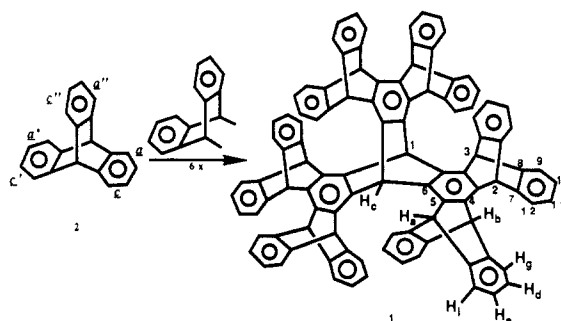
Supertriptycene, C₁₀₄H₆₂¹

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Recently² we analyzed the consequences of fusing 9,10-anthradiyl moieties to the benzenoid bonds of triptycene **2**.³ Twenty-four iptycenes can be generated in this way, the ultimate structure being the pentadecaiptycene³ **1**, with six 9,10-anthradiyl



groups fused across the *a*, *c*, *a'*, *c'*, *a''*, and *c''* bonds of **2**. This exquisite *D*_{3h} molecule (Figure 1) is of interest for several reasons. It possesses three symmetrically located intramolecular cavities, each lined with six benzenoid rings. Therefore **1** should act as a unique host. Also, we anticipated that **1** would be exceptionally thermally stable.^{2,4} Finally, iptycene **1** represents conceptually the first (and also the only possible) stage of symmetric three-dimensional "expansion" of the triptycene core in a manner similar to that recently developed^{5,6} for starburst dendrimers.

We report here a nine-step synthesis of **1** (overall yield 33–43%) that includes an unusual high-yield Diels–Alder reaction between unactivated hydrocarbon participants.

(1) The Chemical Abstracts name is 5,6,11,12,13,18,19,24,25,26,35,40,41,46-tetradecahydro-35,40[1',2']-41,46[1'',2'']-dibenzeno-5,26[1',2']-6,11-[1'',2'']-13,18[1''',2''']-19,24[1''''',2''''']-tetrabenzeno-12,26[6',7']-endo-penta-phenodinaaphtho[2,3-*a*2',3'-*c*]trinaaphthylene. We thank Dr. Kurt Loening and Dr. Joy E. Merritt, Chemical Abstracts Service, for supplying this name.

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(5) (a) Gellman, S.; Petter, R.; Breslow, R. *J. Am. Chem. Soc.* **1986**, *108*, 2388. (b) Breslow, R.; Singh, S. *Bioorg. Chem.* **1988**, *16*, 408.

(6) Characterized by NMR, IR, and mass spectra.

(7) Compound **2** was purified by Sephadex LH-20 chromatography. Anal. Found (calcd for C₂₀H₂₄N₄SZnBr₄·2H₂O) C, 42.41 (42.45); H, 4.55 (4.95); N, 9.55 (9.91); Zn, 10.73 (11.56); Br, 19.81 (19.81). ¹H NMR (CD₃OD): δ 8.25–8.00 (3 H, m), 7.90 (1 H, d, *J* = 7.6 Hz), 7.35 (1 H, dd, *J*_o = 7.1 Hz, *J*_m = 2.1 Hz), 7.05–6.90 (2 H, m), 4.34 (1 H, d, *J* = 12.0 Hz), 4.25–4.10 (1 H, m), 3.92 (1 H, d, *J* = 11.6 Hz), 3.73 (1 H, t, *J* = 12.0 Hz), 3.60–3.30 (1 H, m), 3.25–3.15 (1 H, m), 3.10–2.95 (2 H, m), 2.90–2.80 (1 H, m), 2.56 (3 H, s), 2.35–2.15 (1 H, m), 2.1–1.8 (3 H, m). Compound **3** was purified by Sephadex LH-20 chromatography. Anal. Found (calcd for C₂₃H₂₆N₄SZnBr₂·H₂O) C, 40.55 (40.64); H, 4.72 (4.71); N, 12.64 (12.37); Zn, 8.49 (9.63); Br, 26.18 (23.53). ¹H NMR (CD₃OD): δ 8.15–8.05 (2 H, m), 7.80–7.70 (2 H, m), 7.44–7.25, (3 H, m), 7.40 (1 H, s, H₄ of Im), 7.00 (1 H, s, H₅ of Im), 4.20–4.05 (4 H, m), 3.65–3.45 (2 H, m), 3.25–2.95, (3 H, m), 2.52 (3 H, s, protons of this methyl group exchange with deuteriums of CD₃OD rapidly), 2.40–2.10 (2 H, m), 2.10–1.95 (2 H, m).

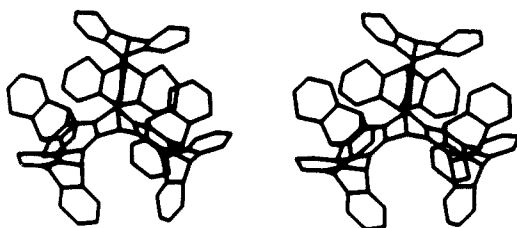
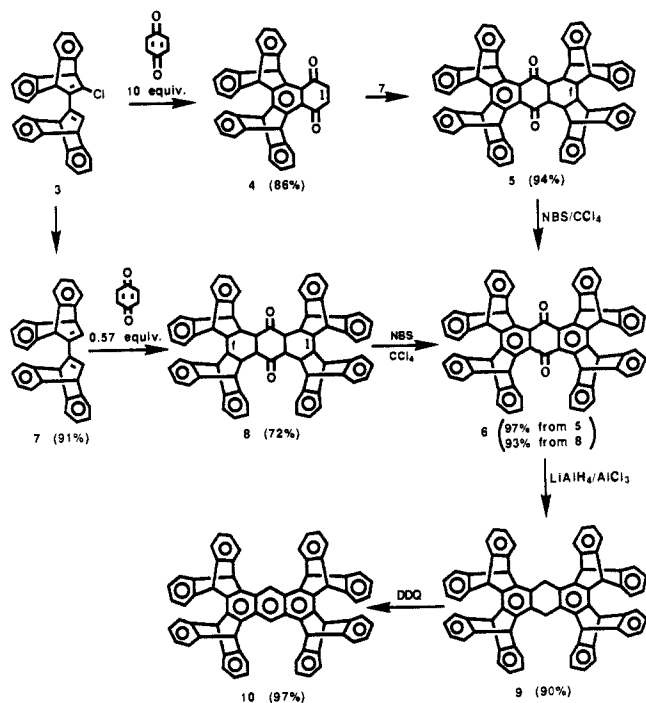


Figure 1. Computer-drawn stereomodel of 1.

Scheme I



Our initial target was anthracene **10** (Scheme I). Readily available chloro diene **3**⁷ was treated with varying ratios of benzoquinone, but the reaction was clean only with a large excess of quinone, in which case the product was naphthoquinone **4**.⁸ The second half of the molecule was attached by cycloaddition of **4** to the nonchlorinated diene **7**,⁹ giving **5** which was readily aromatized to anthraquinone **6** by *N*-bromosuccinimide (NBS). Alternatively, **6** could be prepared from **7** in comparable overall yield by double cycloaddition to quinone to give **8** followed by NBS aromatization.

Anthraquinone **6** was cleanly reduced with 10 equiv of LiAlH₄ and 5 equiv of AlCl₃ to the dihydroanthracene **9** in good yield, and this was subsequently dehydrogenated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in nearly quantitative yield to the desired **10** (yellow, mp >500 °C). This C₇₀H₄₂ hydrocarbon displayed the required six peaks in its ¹H NMR spectrum¹⁰ and twelve peaks in its ¹³C NMR spectrum.¹¹

(7) Shahlai, K.; Hart, H. *J. Am. Chem. Soc.* **1988**, *110*, 7136–7140.

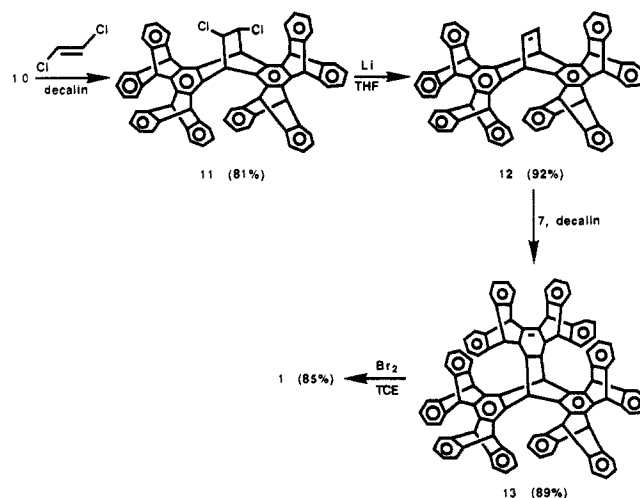
(8) All compounds except **13** gave satisfactory elemental analyses and spectra consistent with the assignments. An accurate analysis was impossible to obtain for **13** due to persistent solvent occlusion⁴ and a tendency to decompose (retro-DA) when heated to remove occluded solvent. This compound did give a satisfactory high-resolution mass spectrum and ¹H and ¹³C NMR spectra.

(9) Shahlai, K.; Hart, H. *J. Org. Chem.* **1989**, *54*, 2615–2620.

(10) (In CD₂Cl₂) δ 6.31 and 6.42 (s, 4 H each, bridgeheads), multiplets centered at 6.97 (16 H), 7.24 (8 H), and 7.54 (8 H) for the four sets of aromatic protons of the "outer" benzenoid rings and a sharp singlet at δ 9.26 (2 H) for the aromatic protons of the anthracene moiety.

(11) (In CD₂Cl₂) δ 49.97 and 50.89 (bridgeheads), and 116.00, 123.40, 123.62, 124.94, 125.10, 125.40, 139.53, 144.97, 145.66, and 146.14 for the aromatic carbons.

Scheme II



Scheme II describes our best route from anthracene **10** to supertritycene. Heating **10** in a 1:1 *trans*-1,2-dichloroethene-decalin mixture (200–205 °C, 68 h) gave adduct **11** as a white solid that was dehalogenated to alkene **12** (20 equiv of Li wire, THF, 72 h reflux).¹²

The supertritycene ring system was assembled via a Diels-Alder reaction between diene **7** and dienophile **12**. Heating 1 mmol of **12** and 1.1 mmol of **7** in 50 mL of decalin at reflux for 8 h gave **13** in 89% yield. Consistent with its C_v symmetry, the ¹³C NMR spectrum of **13** showed eight aliphatic (non-vinyl) carbon signals. The cyclohexene ring of **13** was aromatized in 85% yield by heating with excess bromine in refluxing 1,1,2,2-tetrachloroethane for 4 h.

The D_{3h} symmetry of **1** is evident from its NMR spectra. This C₁₀₄H₆₂ hydrocarbon has only seven magnetically unique types of protons. In tetrachloroethane these appear at δ 5.63 (s, 6 H, H_a), 5.90 (s, 6 H, H_b), 6.60 (s, 2 H, H_c), 6.73–6.79 (m, 24 H, H_d and H_e), 7.16 (d, J = 6 Hz, 12 H, H_f), 7.50 (d, J = 6 Hz, 12 H, H_g).¹³ Similarly, **1** has only 12 magnetically unique carbons. The bridgehead carbons appear at δ 43.46 (2 C, C₁) and 52.55 and 53.01 (6 C each, C₂ and C₃). The aryl carbons of the inner rings appeared at δ 136.74, 136.93, and 137.48 (6 C each, C₄, C₅, and C₆). The nonprotonated carbons of the outer rings appeared at δ 146.76 and 146.96 (12 C each, C₇ and C₈), whereas the protonated carbons appeared at δ 125.46, 126.06, 126.90, and 127.14 (12 C, each, C₉–C₁₂). The simplicity of these spectra leave no doubt as to the structure.

Supertritycene is soluble in tetrachloroethane or in hot decalin or benzonitrile. Under thermogravimetric conditions (N₂ atmosphere) **1** is stable up to 580 °C, where decomposition begins.

Supertritycene is the largest nonpolymeric ityptene synthesized to date. The syntheses outlined here can supply gram quantities for further study.¹⁴

Acknowledgment. We are indebted to the National Science Foundation (Grant CHE 87-12118) and the National Aeronautics and Space Administration (Grant NAG-3-670) for financial support of this research. We thank Dr. Mary Ann Meador (NASA, Cleveland, Ohio) for the thermogravimetric analysis.

(12) For **11**: ¹H NMR (CDCl₃) δ 3.91 (s, 2 H), 5.33 (s, 2 H), 5.77 (s, 2 H), 5.88 (s, 4 H), 5.89 (s, 2 H), 6.77–7.08 (m, 16 H), 7.25–7.59 (m, 16 H); ¹³C NMR (CD₂Cl₂) δ 44.91, 50.15, 50.23, 50.29, 65.88, 77.90, 123.78, 123.87, 123.96, 124.05, 124.19, 124.28, 125.35, 125.66, 125.78, 125.85, 126.01, 127.64, 129.93, 137.81, 138.04, 138.69, 144.81, 145.10, 145.25, 145.31, 145.57. For **12**: ¹H NMR (CDCl₃) δ 5.82 (s, 4 H), 5.87 (s, 4 H), 5.98 (dd, J = 3.7 Hz, <1, 2 H), 6.76 (dd, J = 3.7 Hz, <1, 2 H), 6.80–7.01 (m, 16 H), 7.25–7.54 (m, 16 H); ¹³C NMR (CD₂Cl₂) δ 42.77, 50.12, 50.32, 123.77, 123.93, 124.11, 125.22, 125.64, 125.69, 135.02, 135.95, 140.01, 144.89, 145.13, 145.66, 145.72.

(13) Assignments of H_a vis-a-vis H_b and of the aryl protons are made by comparison with other ityptenes.

(14) **Note Added in Proof:** This manuscript was accepted by the editor on January 16, 1990. Publication was delayed through no fault of the authors.