biogenetic origin of the "unnatural" H14 configuration in contignasterol (1) is of considerable interest.

Experimental Section

Contignasterol (1): obtained as colorless needles from MeOH/H_2O (≈10:1), mp 239–41 °C; FTIR (film) 1719 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 6.21 (bs), 5.94 (bs), 5.72 (bs), 5.16 (bs), 4.53 (bm), 4.50 (bm), 4.34 (bs), 4.16 (bm), 4.04 (bs), 3.88 (bs), 3.78 (bt, J = 10.5 Hz), 3.62 (bs), 3.22 (bt, J = 9.4 Hz), 3.05 (bs), 3.00 (bs), 2.38 (bm), 2.09 (bd, J = 20.0 Hz), 1.13 (s), 0.93 (s) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ 219.4, 219.3, 95.6, 90.4, 75.2, 73.9, 73.8, 70.3, 70.2, 68.6, 68.0, 67.7, 50.7, 50.5, 46.3, 45.8, 45.0, 44.9, 41.3, 41.2, 40.0, 38.8, 38.6, 38.3, 38.2, 36.9, 35.7, 35.5, 34.6, 34.0, 32.5, 32.1, 31.9, 31.8, 23.6, 20.1, 19.6, 19.3, 19.2, 18.9, 18.8, 16.7, 16.7, 14.8 ppm; EIHRMS M^+ m/z 508.3394 ($C_{29}H_{48}O_7$ ΔM −0.6 mmu); EILRMS m/z 508, 490, 472, 457, 447, 408, 319, 264, 246, 221, 203, 155, 119, 109.

Contignasterol Tetraacetate (2). Contignasterol (1) (18.0 mg) was stirred in pyridine (2 mL) and acetic anhydride (2 mL) at room temperature for 18 h. The reagents were removed in vacuo, and the resulting gum was purified using normal-phase HPLC (3:2 ethyl acetate/hexane) to yield the tetraacetate 2 (5.8 mg) and the pentaacetate 3 (≈1 mg). 2: colorless oil; $[\alpha]_D$ +63° (CH_2Cl_2, c 0.34); FTIR (film) 3477, 1748, 1736 cm^{-1}; ^1H NMR see Table I; ^{13}C NMR see Table I; EIHRMS (M^+ − HOAc) m/z 616.3605 ($C_{35}H_{52}O_9$ ΔM −0.6 mmu); EILRMS m/z 616, 556, 513, 496, 436, 123, 60, 43.

Contignasterol pentaacetate (3): colorless oil; ^1H NMR (400 MHz, benzene-d_6) δ 0.75 (d, J = 6.5 Hz, 3 H), 0.76 (d, J = 6.6 Hz, 3 H), 0.77 (d, J = 6.8 Hz, 3 H), 0.94 (s, 3 H), 1.24 (s, 3 H), 1.54 (s, 3 H), 1.80 (s, 3 H), 1.86 (s, 3 H), 1.89 (s, 3 H), 1.95 (s, 3 H), 2.10 (dd, J = 3.4, 12.4 Hz), 2.31 (dd, J = 10.3, 20.0 Hz), 2.39 (bs), 3.32 (m), 5.10 (m), 5.45 (dd, J = 9.0, 12.0 Hz), 5.47 (bs), 5.60 (dd, J = 2.2, 9.0 Hz), 6.54 (dd, J = 9.1, 10.6 Hz).

Contignasterol Reduction Product 4. $NaBH_4$ (21 mg) was added to a solution of contignasterol (1) (12.5 mg) in isopropyl alcohol (10 mL). The reaction mixture was stirred at room temperature for 1 h and quenched with H_2O (10 mL). The resulting suspension was extracted with EtOAc (2 × 10 mL), and the ethyl acetate layer was washed with 1 N HCl (10 mL) and H_2O (10 mL). Purification of the ethyl acetate soluble material using reversed-phase HPLC (25:75 H_2O/MeOH) gave the reduction product 4 (7.6 mg, 61%): white solid.

Reduction Product Pentaacetate 5. Reduction product 4 (7.6 mg) was stirred in pyridine (1 mL) and acetic anhydride (1 mL) at room temperature for 17 h. The reagents were removed in vacuo, and the resulting gum was purified on normal-phase HPLC (1:1 EtOAc/Hex) to give the pentaacetate 5: colorless oil; ^1H NMR (400 MHz, benzene-d_6) δ 0.74 (d, J = 6.8 Hz, H27), 0.76 (d, J = 6.8 Hz, H26), 0.87 (m H23), 1.03 (d, J = 6.8 Hz, H21), 1.04 (s, H19), 1.07 (s, H18), 1.21 (m, H28), 1.25 (m, H1), 1.25 (m, H25), 1.26 (m, H16), 1.48 (m, H23′), 1.59 (s, OAc), 1.60 (m, H2′), 1.62 (m, H28′), 1.63 (m, H5), 1.72 (s, OAC), 1.76 (s, OAc), 1.80 (m, H17), 1.82 (s, OAc), 1.91 (m, H20), 1.99 (m, H8), 2.00 (m, H2), 2.08 (s, OAc), 2.15 (dd, J = 3.6, 7.8 Hz, H14), 3.54 (dd, J = 5.9, 9.4 Hz, H22), 3.82 (bm, H4), 5.07 (dd, J = 8.9, 11.2 Hz, H7), 5.18 (bm, H3), 5.25 (m, H15), 5.32 (dd, J = 8.9, 12.2 Hz, H6), 5.75 (dd, J = 2.2, 9.7 Hz, H29) ppm; EIHRMS (M^+ − HOAc) m/z 660.3871 ($C_{37}H_{56}O_{10}$ ΔM −0.2 mmu); EILRMS m/z 660, 642, 615, 600, 540.

Acknowledgment. Financial support was provided by the Natural Sciences and Engineering Research Concil of Canada and the National Cancer Institute of Canada. The authors wish to thank Professor van Soest for identifying the sponge and M. LeBlanc and C. Arneson for assisting the collection.

Registry No. 1, 137571-30-3; 2, 137571-31-4; 3, 137571-32-5; 4, 137571-33-6; 5, 137571-34-7.

Supplementary Material Available: ^1H and ^{13}C NMR spectra for contignasterol (1) and the tetraacetate 2 (4 pages). Ordering information is given on any current masthead page.

C- and Z-Shaped Ditopic Cavitands, Their Binding Characteristics, and Monotopic Relatives[1]

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Readily available octol 1, when treated with 3 mol of CH_2ClBr, gave hexol 2 (3%), tetrol 3 (7%), diol 4 (17%), and tetra-bridged 5 (10%). The tetrol and diol served as starting materials for preparing mixed-bridged systems. Diol 4 reacted with 2,3-dichloroquinoxaline (7) to give 7% of cavitand 8, whereas tetrol 3 reacted with only one of the 2 mol of quinoxaline 7 to give the chiral diol 9 (18%). When 2 mol of diol 4 were treated with 1 mol of fluoranil (6), the mixture of 42% of Z-shaped 10 (**Z-10**) and 12% of C-shaped 10 (**C-10**) produced was easily separated. The crystal structures of **4**·$CHCl_3$·H_2O, **C-10**·3CH_3CN·CH_2Cl_2, **Z-10**·4$CH_3CO_2CH_2CH_3$, **Z-10**·4$CH_3COCH_2CH_3$, and **Z-10**·6$C_6H_5NO_2$ were determined and found to resemble what was predicted from molecular model examination. When 1 mol of diol 4 was mixed with tetrachlorotetraazaanthracene 12, a 16% yield of what is probably **Z-11** was obtained. One-to-one association constants of **C-10** in CD_2Cl_2 at 21 °C were determined by ^1H NMR titrations with guests as follows: $C_6D_5NO_2$ (K_a = 0.6 M^{-1}), $C_6D_5CD_3$ (K_a = 1.8 M^{-1}), p-$CD_3C_6D_4CD_3$ (K_a = 1.6), and $CH_3COCH_2CH_3$ (K_a = 1.2 M^{-1}). Attempts to detect binding failed with 2-butyne, 2-pentyne, and methylcyclohexane, although molecular model examination suggested that all seven of the above guests are complementary to the highly preorganized ditopic cavity of **C-10**.

Previous papers in this series established that octols such as 1 (Chart 1) were readily synthesized from a variety of aldehydes and resorcinol in high yields.[2,3] The conformational mobilities of their configurationally homogeneous all-syn isomer (see 1) were reduced by bridging the four sets of proximate oxygens with four units such as CH_2,

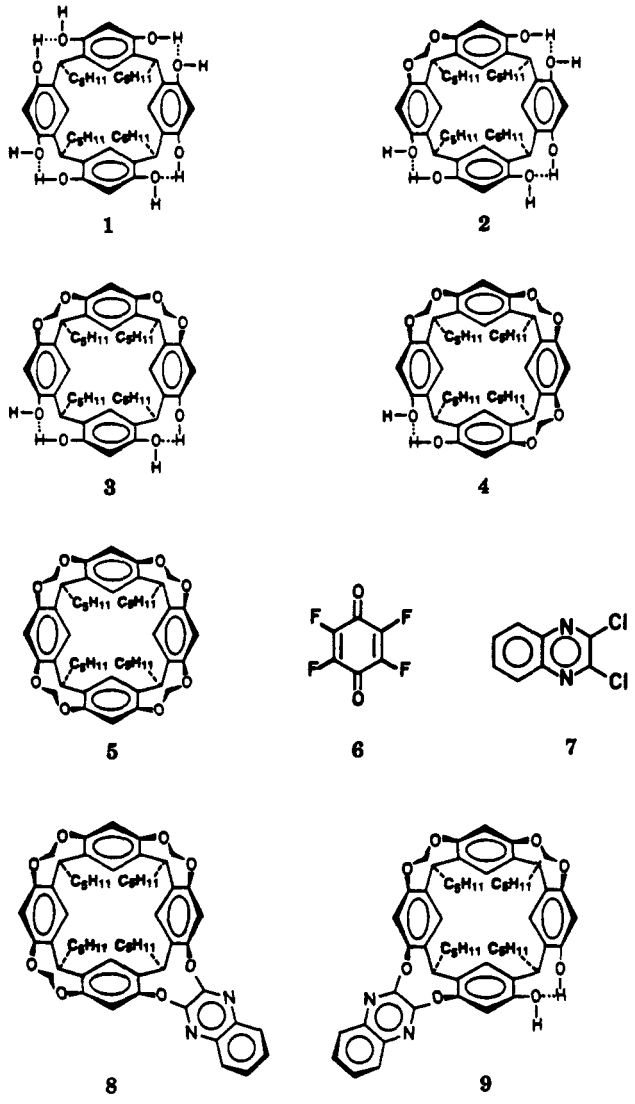
(1) (a) Host–Guest Complexation. 61. (b) We warmly thank the National Science Foundation for Grant Number CHE 88 02800 and L. A. Tunstad thanks the National Institutes of Health for Predoctoral Fellowship NIH NIGMS-MARC Grant F-31, GM 10277.

(2) Hogberg, A. G. S. *J. Am. Chem. Soc.* **1980**, *102*, 6046–6050.

(3) Tunstad, L. M.; Tucker, J. A.; Dalcanale, E.; Weiser, J.; Bryant, J. A.; Sherman, J. C.; Helgeson, R. C.; Knobler, C. B.; Cram, D. J. *J. Org. Chem.* **1989**, *54*, 1305–1312, and references therein.

0022-3263/92/1957-0528$03.00/0

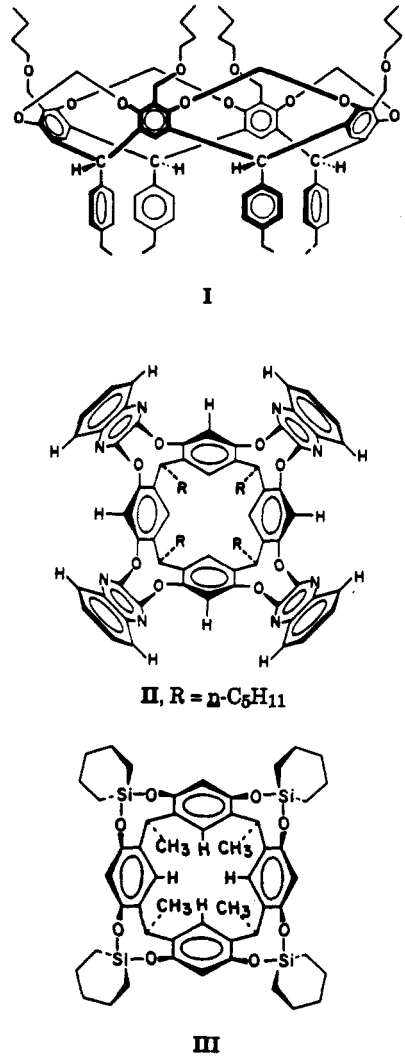
Chart I



$(CH_2)_2$, $(CH_2)_3$,[4,5] 2,3-quinoxaline, 2,3-pyrazine,[6b] or $Si(R)_2$[5,7] to give cavitands capable of weakly binding small guests. Examples are host systems **I**, **II**, and **III** (Chart II).

Two cavitands (**5**) were subsequently bonded to one another through their four aryl-rim positions with four CH_2SCH_2 or OCH_2O groups to give roughly spherical carceplexes in which one or two solvent molecules were incarcerated in their enforced inner phase, as in compounds **IV**[8] and **V**[9] (Chart III). When three OCH_2O interhemispheric bridges based on **5** were employed, hemicarceplexes such as **VI** were formed, whose guest (prisoner) molecules could escape their constrictive binding at high temperatures. New guests of sizes complementary to the shell opening and inner phase then were introduced at high temperatures using the mass law to provide new

Chart II



stable hemicarceplexes held together by constrictive binding.[10]

Attempts to synthesize carceplexes (e.g., **VII**) (Chart IV) by 8-fold bridging reactions between 2 mol of an octol such as **1** and 4 mol of either fluoranil (**6**) or tetrachlorotetraazaanthracene **12**[11] produced only intractable products.[12] We therefore assumed the more modest strategy of first preorganizing the bowls with three intrahemispheric OCH_2O bridges as in **4** and then cementing two bowls together through a single interhemispheric aryl bridge as in **C-10** and **C-11**. Since good yields had been observed in the preparation of **IV**–**VI**, we hoped that the covergent C-shaped diastereomers of **10** and **11** would dominate over the divergent Z-shaped diastereomers of **10** and **11** in the interhemispheric bridging reaction.

Results and Discussion

Syntheses. When octol **1**[3] was submitted to the bridging reaction with CH_2ClBr–K_2CO_3–$(CH_3)_2SO$, the products after silica gel chromatography were monobridged hexol **2** (3%), A,B-di-bridged tetrol **3** (7%), tribridged diol **4** (17%), and tetra-bridged material **5** (10%).

(4) Cram, D. J.; Karbach, S.; Kim, H.-E.; Knobler, C. B.; Maverick, E. F.; Ericson, J. L.; Helgeson, R. C. *J. Am. Chem. Soc.* **1988**, *110*, 2229–2237.
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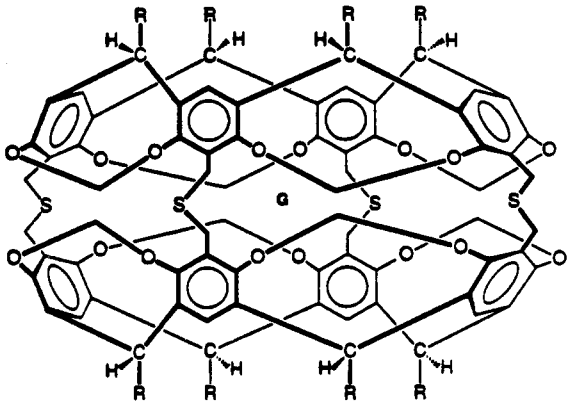
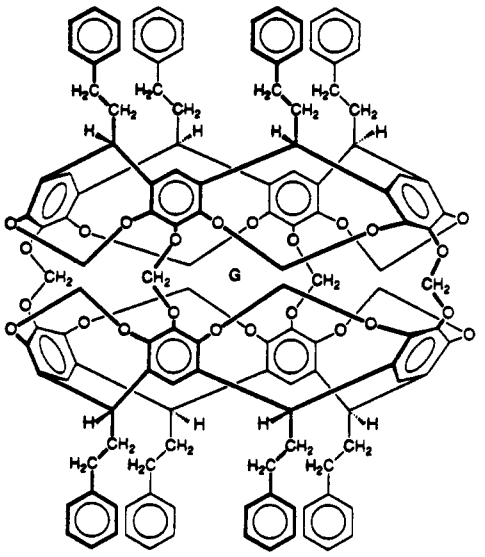
(9) Sherman, J. C.; Knobler, C. B.; Cram, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 2194–2204.
(10) (a) Tanner, M. E.; Knobler, C. B.; Cram, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 1659–1660. (b) Cram, D. J.; Tanner, M. E.; Knobler, C. B. *J. Am. Chem. Soc.* **1991**, *113*, 7717–7727.
(11) Jadamus, H.; DeSchryver, F.; DeWinter, W.; Marvel, C. S. *J. Polym. Sci., A-1* **1966**, *4*, 2831–2842.
(12) Dalcanale, E.; Cram, D. J. Unpublished results.

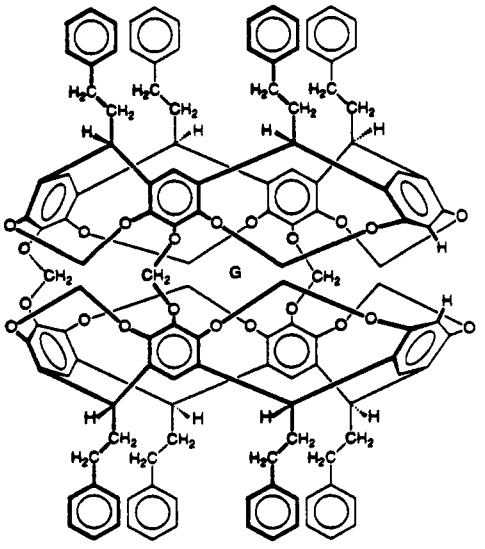
Chart III



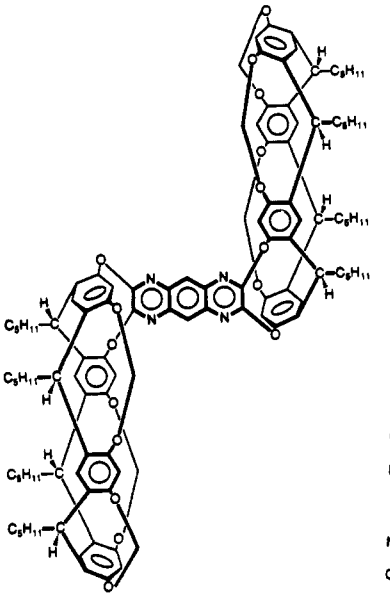
IV, R = n-C_5H_{11}



V



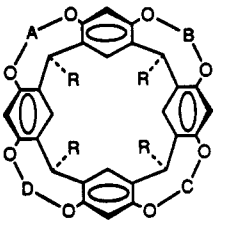
VI



Z-11

12

This yield pattern suggests that the fourth methylene bridge is introduced more slowly than the third. For determination of whether two different kinds of intrahemispheric bridges could be introduced into the same molecule, diol **4** was treated with 2,3-dichloroquinoxaline–Cs_2CO_3–$(CH_3)_2SO$ to give fully bridged cavitand **8** (7%). When tetrol **3** was similarly treated with 2 mol of the 2,3-dichloroquinoxaline, diol **9** (18%) was produced. Again, the fourth bridge appeared to enter the molecule more slowly than the third. An earlier paper reported that when octols such as **1** were treated with 4 mol of 2,3-dichloroquinoxaline, a mixture of tri- and tetra-bridged material resulted.[6b] As the conformationally mobile octol **1** becomes progressively more rigid with additional bridges, the remaining diol pairs appear to become less adaptable to the transition states required for bridging. Diol **9** is distinguished as being the first cavitand of this type to be chiral, its dissymmetry being due to its aryl's inability to ring invert and to the three types of substituents on this molecule, namely, OCH_2O, O,O-disubstituted quinoxaline, and OH···OH. Structure **VIII** indicates the convention we use in referring to bridging patterns.

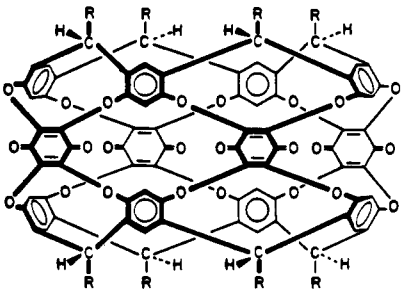


VIII

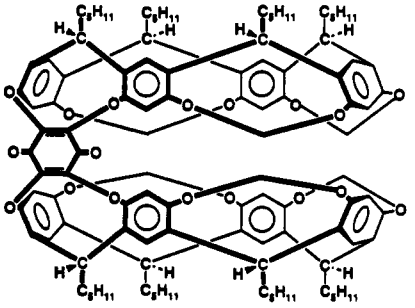
The conversions of diol **4** with fluoranil (**6**) to a mixture of **C-10** and **Z-10** were studied to maximize the yield of both isomers, particularly the more interesting **C-10** diastereomer. The highly reactive fluoranil[13] was added as a solid in portions to stirred mixtures of **4** and various bases and solvents under an atmosphere of argon. The solvents used were $(CH_2)_4O$, $(CH_3)_2NCHO$, $(CH_3)_2NCOCH_3$, and $(CH_3)_2SO$, and the bases were Li_2CO_3, Na_2CO_3, Cs_2CO_3, and $CaCO_3$. In the solvent–base combinations

(13) Patai, S., Ed. *The Chemistry of the Quinonoid Compounds*; John Wiley & Sons: New York, 1974; Part 1, Chapter 17.

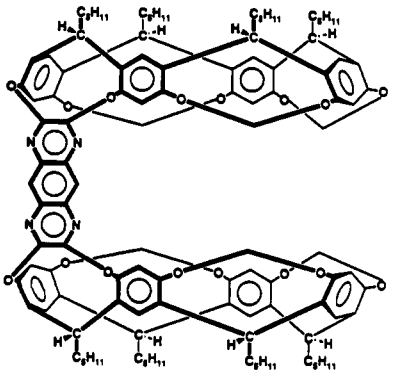
Chart IV



VII, R = n-C_5H_{11}



C-10



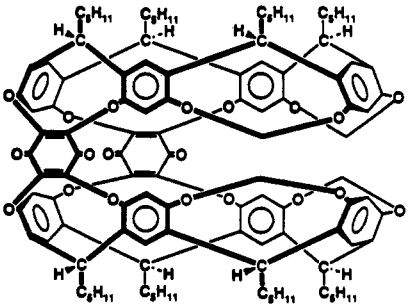
C-11

tried, the sums of the yields of the two isomers varied from 15 to 56% and **Z-10** dominated over **C-10** in the products by factors that ranged from 2 to 20. The two isomers were easily separated by silica gel chromatography, with the C-shaped isomer having the longer retention time (R_f 0.30 vs R_f 0.04). The yields of the desired **C-10** were maximal with $(CH_3)_2SO$–Na_2CO_3 (42% **Z-10** and 12% **C-10**) and $(CH_3)_2NCOCH_3$–Na_2CO_3 (47% **Z-10** and 9% **C-10**). The identity of each isomer was established by crystal structure determination (see next section).

Attempts were made to convert A,B-tetrol **3** to the diquinone-bridged compound **IX** with 2 mol of fluoranil (**6**). Unlike its Z isomer, which could not be constructed with Corey–Pauling–Koltun (CPK) molecular models, those of **IX** appear unstrained. Unfortunately, only polymeric materials resulted.

In an attempt to prepare **C-11**, diol **4** was treated with half a mole of tetrachlorotetraazaanthracene **12**[11] in Na_2CO_3–$(CH_3)_2SO$ at 60–70 °C. The single product isolated (16%) is tentatively assigned structure **Z-11**, based on its chromatographic behavior, which is similar to that of **Z-10**. Attempts to obtain crystals of **11** suitable for crystal structure determination failed.

Crystal Structures. Chart V provides the results of crystal structure determinations of caviplexes **4**·$CHCl_3$·H_2O (R = 0.08), **C-10**·$3CH_3CN$·CH_2Cl_2 (R = 0.21), **Z-10**·$4CH_3CO_2CH_2CH_3$ (R = 0.17), **Z-10**·$4CH_3COCH_2CH_3$ (R = 0.14), and **Z-10**·$6C_6H_5NO_2$ (R = 0.13). In the crystal structure of **4**·$CHCl_3$·H_2O, the host contains a shallow bowl, one of whose two proximate hydroxyl groups is intermolecularly hydrogen bonded to an interstitial water molecule. The O to O distance of the two OH groups is 2.76 Å, longer than those for the three O to O distances for the three covalent bridges of **4**, which averaged 2.35 Å. Into the bowl is thrust one Cl atom of the $CHCl_3$ guest, the host–guest relationship resembling that observed in the crystal structure of the caviplex formed from the analogue of **5**·CH_2Cl_2, in which four methyl groups are substituted for the four pentyl groups of **4**.[4] The water molecule hydrogen bonds to one O of an OH group and to an oxygen of another cavitand (H···O are 1.60 and 1.84 Å, respectively, and O_{water}···O are 2.62 and 2.82 Å, respectively).



IX

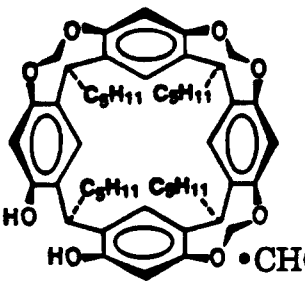
In the three crystal structures of **Z-10** (Chart V), the solvent is disordered and is omitted, although it is clear that the cavity of each bowl is occupied. In the structure of **C-10**·$3CH_3CN$·CH_2Cl_2, a chlorine of a CH_2Cl_2 guest molecule inserts into one of the two bowls, while a CH_3 of a CH_3CN is inserted into the other bowl. Two additional CH_3CN molecules are packed between each set of four pentyl groups that occupy the polar regions of the hemispheres.

An interesting question applicable to all four crystal structures is the angle between the two normals defined by the plane of the quinone and the plane formed by the eight oxygens of each bowl moiety. In CPK models of both the C and Z isomers, the angle appears to be just a little less than 90°. In **C-10**·$4CH_3CN$·CH_2Cl_2, the angles for each of the two bowls are 88 and 87°, the angle for each of the bowls in **Z-10**·$4CH_3CO_2CH_2CH_3$ is 89.5°, in **Z-10**·$4CH_3COCH_2CH_3$ is 89.4°, and for each of the two bowls in **Z-10**·$6C_6H_5NO_2$ is 98.3°. Each of these three **Z-10** molecules of the crystal structures is centrosymmetric. There is enough flexibility in these bond angles to indicate that hypothetical structures such as **VII** and **IX** should be very little strained, a conclusion also derived from CPK molecular model examination. Generally, the *bowl dimensions* of depth, width, and breadth are very close to one another in the crystal structures of **4**, **C-10**, **Z-10**, and the analogues of **5**, which contain four OCH_2O bridges.[4]

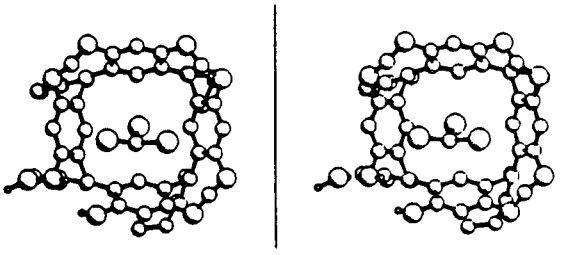
The limited potential for conformational flexibility of host **Z-10** was indicated by the relative insensitivity of its solution ^1H NMR spectra to temperature change. A sample of **Z-10** dissolved in $CDCl_3$ was cooled to −50 °C, and the spectral changes from 25 °C to −50 °C were insignificant (>0.1 ppm).

Solubility Properties of C-10 and Z-10. Both isomers of **10** are soluble in CH_2Cl_2, $CHCl_3$, $C_6H_5NO_2$, $C_6H_5CH_3$, warm C_6H_6, warm EtOAc, and warm $CH_3COCH_2CH_3$. However, **Z-10** dissolved faster in all solvents than did **C-10**. Both hosts were slightly soluble in CH_3COCH_3. Unlike **C-10**, **Z-10** is soluble in CCl_4, $(CH_2)_4O$, and hot

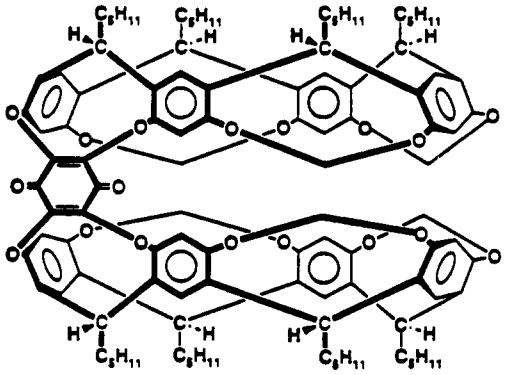
Chart V. Line Structures and Stereoviews of Crystal Structures



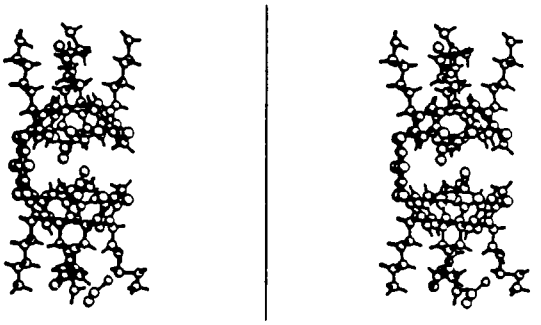
$4\bullet CHCl_3\bullet H_2O$



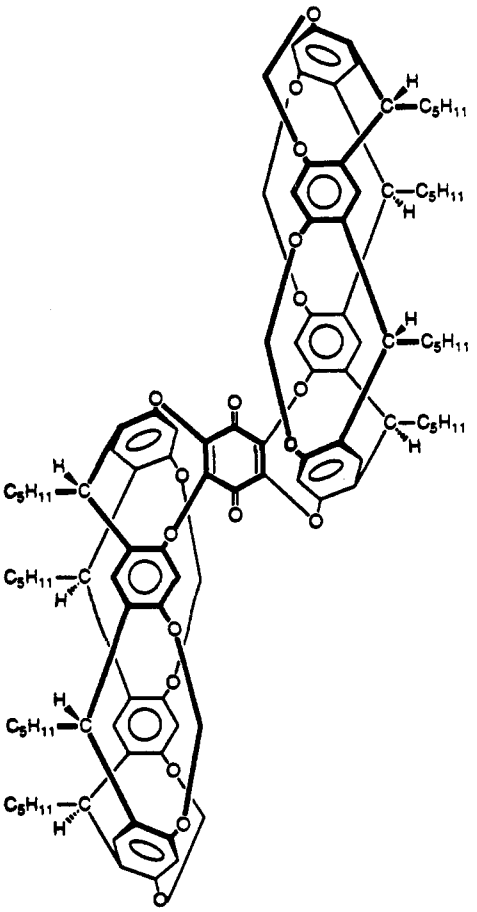
$4\bullet CHCl_3\bullet H_2O$



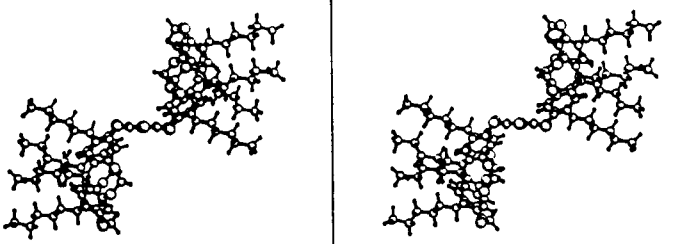
$C\text{-}10\bullet 3CH_3CN\bullet CH_2Cl_2$



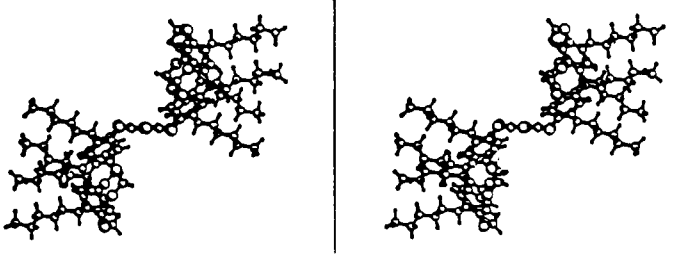
$C\text{-}10\bullet 3CH_3CN\bullet CH_2Cl_2$



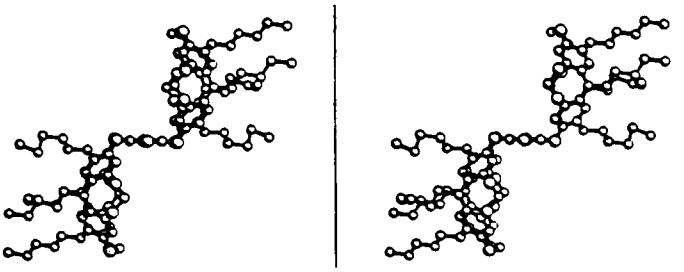
Z-10



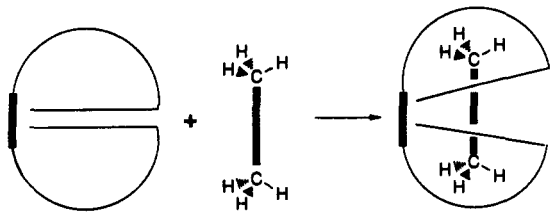
$Z\text{-}10\bullet 4CH_3CO_2CH_2CH_3$



Z-10 of $Z\text{-}10\bullet 4CH_3COCH_2CH_3$



Z-10 of $Z\text{-}10\bullet 6C_6H_5NO_2$



14 guest 14•guest

Figure 1. Visualized mode of binding in C-10·*p*-xylene and other caviplexes.

$(CH_3)_2SO$, whereas **C-10** is soluble in warm C_6H_5Br and *p*-$CH_3C_6H_4CH_3$.

Binding Properties of C-10 and Z-10. Examination of CPK molecular models of **C-10** suggested that $C_6H_5NO_2$, $C_6H_5CH_3$, *p*-$CH_3C_6H_4CH_3$, $CH_3COCH_2CH_3$, $CH_3C{\equiv}CCH_3$, $CH_3C{\equiv}CCH_2CH_3$, and equatorial $CH_3CH(CH_2)_5$ are nicely complementary to the cavity, with the long axis of the guest aligned with that of the host, as in the drawing of Figure 1. Accordingly, ^1H NMR titration experiments were carried out for **C-10** binding $C_6D_5NO_2$, $C_6D_5CH_3$, *p*-$CD_3C_6D_4CD_3$, and $CH_3COCH_2CH_3$, which of the seven examined were the only ones that gave detectable binding. Although CCl_4 would have been the solvent of choice for the experiments,[5] **C-10** was not soluble enough in CCl_4, and CD_2Cl_2 was used as solvent. Benesi–Hildebrand[14] treatment of the titration data involved eq 1, in which δ_{obs} is

$$\frac{1}{(\delta_{obs} - \delta_H)} = \frac{1}{\Delta\delta} = \frac{1}{K_a(\delta_{HG} - \delta_H)}\frac{1}{[G]_0} + \frac{1}{(\delta_{HG} - \delta_H)} \quad (1)$$

the observed signal of host protons in the presence of guest, δ_H is the signal of the host molecule with no guest present, δ_{HG} is the signal for the complex, K_a is the association constant, and $[G]_0$ is the initial concentration of the guest. A plot of the inverse of the observed shift difference ($\Delta\delta$ values found for each guest concentration) versus $1/[G]_0$ permits the calculation of K_a from the slope and the intercept. Because the guest concentration (38–2000 mM) is much greater than the host concentration (~4 mM), the reduction of the guest concentration due to host–guest complexation was disregarded. Table I lists the $\Delta\delta$ values obtained at each guest concentration using different proton indicators in the host. The resulting K_a values plus their correlation coefficients and the K_a averaged value for each guest are also found in Table I. All experiments were conducted at 21 °C. The host protons involved are labeled in structure **13**. The protons selected for estimating the binding constants were those which shifted the most upon guest addition. Generally, these are the protons closest to the cavity, H^a, H^b, H^c, H^d, H^e, and H^f.

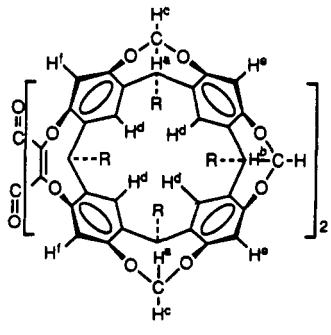


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Table I. Maximum Ranges of Chemical Shifts ($\Delta\delta$) in 400-MHz ^1H NMR Spectra of Selected Host Protons at 4.0 mM in CD_2Cl_2 at 21 °C with Maximum Changes in Guest Concentrations, the Resulting K_a Values, the Number of Points, Correlation Coefficients, and Average K_a Values

guest kind	guest concn range Δ[M]	host proton	max Δδ[a] (ppm)	no. pts	K_a (M^{-1})	correl coeff	K_a^{av} (M^{-1})
$C_6D_5NO_2$	1.981	H^a	0.066	5	0.77	0.992	
		H^b	0.066	5	0.27	1.000	0.59
		H^c	0.076	5	0.73	1.000	
$C_6D_5CD_3$	0.616	H^a	0.046	7	1.53	0.950	
		H^c	0.030	6	3.40	0.980	1.8
		H^d	0.067	7	0.36	0.985	
p-$CD_3C_6D_4CD_3$	1.360	H^a	0.716	7	1.35	0.983	
		H^b	−0.102	6	2.90	0.990	1.6
		H^d	0.240	6	1.13	0.996	
		H^e	0.223	7	0.982	0.992	
$CH_3COCH_2CH_3$	1.284	H^b	0.276	7	1.89	1.000	
		H^d	−0.031	6	0.37	0.987	1.24
		H^f	0.081	7	1.45	1.000	

[a] Negative values indicate upfield shift, positive values downfield shift.

Qualitative ^1H NMR binding studies were carried out with **Z-10** using the above technique with $C_6D_5CD_3$, $C_6D_5NO_2$, or CD_3CN as potential guests at 21 °C in CCl_4, a solvent which is a much poorer competitor for binding host than the CD_2Cl_2 used for **C-10**.[5] The total number of equivalents of guest added per equivalent of host ranged from 685 to 1466, compared to 154 to 500 employed with the titrations of **C-10** in CD_2Cl_2. The largest chemical shift changes with added guest observed in these control experiments were less than 0.01 ppm.[15] *Thus a condition for observable binding appears to be the ability of the two hemispheric binding sites to be proximate as in* ***C-10*** *rather than remote as in* ***Z-10***. The cooperativity of the two concave surfaces as suggested in Figure 1, drawing **14·guest**, appears necessary for bidning.

The K_a^{av} association constants (Table I) varied as follows: $C_6D_5NO_2$, 0.59 M^{-1}; $C_6D_5CD_3$, 1.8 M^{-1}; *p*-$CD_3C_6D_4CD_3$, 1.6 M^{-1}; $CH_3COCH_2CH_3$, 1.2 M^{-1}. Although the factors by which these averaged values differ are smaller than the factors by which in extreme cases the individual averaged K_a values differed, the trends are meaningful. The poorest binding guest is $C_6D_5NO_2$, which may reflect both its relatively poor shape and the fact that both the guest and the quinone-bridging groups are π acids. The best binding groups are $C_6D_5CD_3$ and *p*-$CD_3C_6D_4CD_3$, which are both complementary in shape and are π-bases. The conformationally mobile $CH_3COCH_2CH_3$ is a surprisingly strong binder.

Summary. Both C- and Z-shaped hosts (**C-10** and **Z-10**) have been prepared by rigidly bridging two bowl-shaped cavitands with one 1,4-benzoquinone unit. The identity of the isomers was established by crystal structure determination. Studies of **C-10** and **Z-10** showed that the two proximate bowls in **C-10** acted cooperatively to bind complementary guests, whereas **Z-10**, whose bowl parts are remote, showed no evidence of binding.

Experimental Section

General. Dry tetrahydrofuran (THF) and diethyl ether were prepared by distilling them from sodium benzophenone ketyl prior to use. Purchased chemicals were used as received or, when indicated, purified according to Perrin and Perrin.[16] Chroma-

(14) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707.

(15) Recently, R. Breslow and S. Chung [*J. Am. Chem. Soc.* **1990**, *112*, 9659–9660] attached two cyclodextrins together with two bridges between adjacent oxygens and observed greatly enhanced guest binding for the syn vs the anti host in water as solvent.

tography was performed with 0.063–0.200-mm silica gel (E. Merck). Preparative thin-layer chromatography was performed on E. Merck glass-backed plates. Melting points were recorded on a Mel-Temp apparatus in open capillaries and are uncorrected. Fast atom bombardment (FAB) mass spectra were recorded on a ZAB SE instrument using *m*-nitrobenzyl alcohol (NOBA) as the matrix.

2,20:3,19-Dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino-[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]bis[1,3]benzodioxocin, 1,21,23,25-Tetrapentyl- (Stereoisomer 5). Octol 1[3] (4.1 g, 5.3 mmol) was dissolved in 250 mL of dry $(CH_3)_2SO$ under argon to yield an orange solution. Ground K_2CO_3 (7.5 g, 54.3 mmol, 10.2 equiv) when added to this mixture produced a deep red color. The reaction was heated in an oil bath at 60 °C, and $BrCH_2Cl$ (2.19 g, 16.93 mmol, 3.2 equiv) was added via syringe all at once. The reaction was stirred for 24 h and then cooled to 25 °C, poured into 1 L of brine, stirred, filtered, washed with several portions of water, and air dried. The tan powder was dissolved in CH_2Cl_2 and chromatographed on a medium pressure silica column. Gradient elution (CH_2Cl_2, 0–3% CH_3OH) provided 400 mg (~10%) of tetra-bridged **5** (R_f = 0.36, CH_2Cl_2), 600 mg (~17%) of tri-bridged **4**, 50 mg (~7%) of di-bridged **3** (AB), and 25 mg (~3%) of mono-bridged **2**. Compound **5**: mp 226–228 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K, H_i identifies hydrogens pointing inward toward the cavity, and H_o those pointing outward from the cavity) δ 0.91 (t, *J* = 6.8 Hz, 12 H, $(CH_2)_4CH_3$), 1.24–1.50 (bm, 24 H, $CH_2(CH_2)_3CH_3$), 1.58 (bs, H_2O), 2.15–2.27 (m, 8 H, CH_2-$(CH_2)_3CH_3$), 4.43 (d, *J* = 7.4 Hz, 4 H, -OCH_iH_oO-), 4.72 (t, *J* = 8.0 Hz, 4 H, ArCH), 5.74 (d, *J* = 7.4 Hz, 4 H, -OCH_iH_oO-), 6.48 (s, 4 H, ArH), 7.11 (s, 4 H, ArH); MS (FAB, $CHCl_3$) *m/e* 816.5 (M^+, 100), 745.5 (M^+ – 71 (pentyl), 9). Anal. Calcd for $C_{52}H_{64}O_8$ (dried at 10^{-5} Torr, 100 °C, 10 h): C, 76.44; H, 7.89. Found: C, 76.50; H, 8.07.

2,18-Methano-20*H*,22*H*,24*H*-dibenzo[*d*,*d*′][1,3]dioxocino-[5,4-*i*:7,8-*i*′]bis[1,3]benzodioxocin-3,17-diol, 20,22,24,25-Tetrapentyl- (Stereoisomer 4). This compound was prepared by the above procedure for preparing **5**. **4**: mp 147–150 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 0.87–0.95 (m, 12 H, $C_4H_8CH_3$), 1.27–1.41 (m, 24 H, $CHCH_2(CH_2)_3CH_3$), 2.14–2.24 (m, 8 H, $CHCH_2C_4H_9$), 4.29 (t, *J* = 3.9 Hz, 1 H, Ar_2CH below hydroxyls), 4.36 (d, *J* = 3.6 Hz, 1 H, -OCH_iH_oO- center bridge), 4.46 (d, *J* = 3.6 Hz, 2 H, -OCH_iH_oO- two outer bridges), 4.68 (dt, *J* = 3.9 Hz, 3 H, Ar_2CH adjacent to -OCH_2O- bridges), 5.71 (d, *J* = 3.6 Hz, 1 H, -OCH_iH_oO- center bridge), 5.73 (d, *J* = 3.6 Hz, 2 H, -OCH_iH_oO- outer bridges), 6.37 (s, 2 H, ArH ortho to O's, adjacent to hydroxyls), 6.48 (s, 2 H, ArH ortho to O's, distant from hydroxyls), 7.09 (s, 2 H, ArH meta to O's, distant from hydroxyls), 7.16 (s, 2 H, ArH meta to O's, adjacent to hydroxyls), 8.05 (bs, 1.7 H(2), OH); MS (FAB, 5 kV) *m/e* 806.5 (M^+ + 2, 24), 805.5 (M^+ + 1, 70), 804.5 (M^+, 100), 733.4 (M^+ – 71 (pentyl), 58). Anal. Calcd for $C_{51}H_{64}O_8$ (dried at 10^{-5} Torr, 100 °C, 10 h): C, 76.09; H, 8.01. Found: C, 76.20; H, 8.09.

2,14-(Methano[1,3]benzenomethano)-16*H*,18*H*-benzo[1,2-*d*:5,4-*d*′]bis[1,3]benzodioxocin-3,13,23,25-tetrol, 16,18,19,26-Tetrapentyl- (Stereoisomer 3). This compound was prepared by the procedure for preparing **5** and **4**. **3**: mp 150–153 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 0.88–0.94 (m, 12 H, $C_4H_8CH_3$), 1.20–1.50 (m, 24 H, $CHCH_2(CH_2)_3CH_3$), 2.05–2.40 (m, 8 H, $CHCH_2C_4H_9$), 4.25 (bt, 2 H, Ar_2CH below hydroxyls), 4.40 (d, *J* = 3.6 Hz, 2 H, -OCH_iH_oO-), 4.69 (t, *J* = 3.8 Hz, 2 H, Ar_2CH adjacent to -OCH_2O- bridges), 5.69 (d, *J* = 3.6 Hz, 2 H, -OCH_iH_oO-), 6.31 (s, 2 H, ArH), 6.34 (s, 1 H, ArH), 6.46 (s, 1 H, ArH), 6.98 (s, 1 H, ArH), 7.17 (bs, 3 H, ArH), 8.02 (bs, 3 H(4), OH); MS (FAB, 5 kV) *m/e* 793 (M^+, 25), 792 (M^+ – 1, 30), 721 (M^+ – 71 (pentyl), 100). Anal. Calcd for $C_{50}H_{64}O_8$ (dried at 10^{-5} Torr, 100 °C, 10 h): C, 75.73; H, 8.13. Found: C, 75.66; H, 8.29.

2,10-(Methano[1,3]benzenomethano)-12*H*-dibenzo[*d*,*g*]-[1,3]dioxocin-3,9,17,19,24,26-hexol, 12,13,20,27-Tetrapentyl (Stereoisomer 2). This compound was prepared by the procedure used to prepare **5**, **4**, and **3**. **2**: mp 213–217 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 0.85–0.96 (m, 12 H, $C_4H_8CH_3$), 1.15–1.42 (bs, 24 H, $CHCH_2(CH_2)_3CH_3$), 2.03–2.32 (bm, 8 H, $CHCH_2C_4H_9$), 4.13–4.40 (m, 4 H, ArCH, -OCH_iH_oO-), 4.69 (t, *J* = 3.9 Hz, 1 H, ArCH), 6.71 (d, *J* = 3.7 Hz, 1 H, -OCH_iH_oO-), 6.25 (s, 2 H, ArH), 6.38 (s, 2 H, ArH), 7.07 (s, 2 H, ArH), 7.19 (s, 2 H, ArH), 8.7–9.2 (bd, ~3 H(6), OH); MS (FAB, 5 kV) *m/e* 781 (M^+ + 1, 15), 780 (M^+, 22), 709 (M^+ – 71 (pentyl), 100). Anal. Calcd for $C_{49}H_{64}O_8 \cdot {}^3/_2H_2O$ (dried at 10^{-5} Torr, 100 °C, 10 h): C, 72.83; H, 8.36. Found: C, 72.59; H, 8.22.

4,14:5,13-Dimetheno-6*H*,8*H*,10*H*,12*H*-1,3-dioxocino-[5‴,4‴:8″,9″][1,3]benzodioxocino[5″,4″:8′,9′][1,3]benzodioxocino[5′,4′:9,10][1,4]benzodioxocino[2,3-*b*]quinoxaline, 6,8,10,12-Tetrapentyl- (Stereoisomer 8). Under an argon atmosphere, tri-bridged diol **4** (0.197 g, 0.245 mmol) was dissolved in 70 mL of anhydrous $(CH_3)_2SO$, 0.26 g (0.79 mmol) of Cs_2CO_3 was added, and then dichloroquinoxaline **7** (0.063 g, 0.315 mmol) was added all at once. The reaction mixture was heated to 70 °C in an oil bath and stirred for 2 days, at which time the TLC behavior of a sample showed no difference from that of 1 day. The reaction mixture was cooled to 25 °C, poured into 1 L of brine, stirred, and filtered (medium frit). The resulting solid was washed with several portions of H_2O and air dried. The brown powder was dissolved in CH_2Cl_2 and placed on a 2-mm-thick layer silica plate and eluted with CH_2Cl_2. The first fraction was isolated and provided 0.0152 g (1.63×10^{-5} mol, 7%) of **8**: mp (fast) 124–140 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 0.85–1.0 (t, *J* = 6.8 Hz, 12 H, $C_4H_8CH_3$), 1.22–1.55 (bm, 24 H, $CH_2C_3H_6CH_3$), 1.56 (s, ~3 H, H_2O), 2.1–2.4 (bm, 8 H, $CH_2C_4H_9$), 4.24–4.30 (overlapping doublets, *J* = 7.4 Hz, 3 H, -OCH_iH_oO-), 4.62–4.77 (overlapping triplets, *J* = 8.2 Hz, 3 H, ArCH), 5.63 (d, *J* = 7.4 Hz, 1 H, -OCH_iH_oO-), 5.70–5.78 (doublet with triplet buried, *J* = 7.4 Hz for doublet, total of 4 H, 3 -OCH_iH_oO- and 1 ArCH), 6.39 (s, 2 H, ArH), 7.11 (s, 2 H, ArH), 7.18 (s, 2 H, ArH), 7.38 (s, 2 H, ArH), 7.88 (quinoxaline AA′BB′ pattern center, 4 H, ArH); MS (FAB, CH_2Cl_2) *m/e* 933 (M^+ + 2, 55), 932 (M^+ + 1, 100), 931 (M^+ – 1, 56). Anal. Calcd for $C_{59}H_{66}O_8N_2$ (dried at 10^{-5} Torr, 100 °C, 10 h): C, 76.10; H, 7.14; N, 3.01. Found: C, 75.95; H, 7.18; N, 2.97.

3,11-Methano-5*H*,7*H*,9*H*-benzo[5,6][1,3]benzodioxocino-[5″,4‴:8′,9′][1,3]benzodioxocino[5′,4′:9,10][1,4]benzodioxonino[2,3-*b*]quinoxaline-2,12-diol, 5,7,9,30-Tetrapentyl- (Stereoisomer 9). A mixture of 0.148 g (0.186 mmol) of dry AB-bridged tetrol **3** and Cs_2CO_3 (0.242 g) was stirred in an atmosphere of argon. Anhydrous $(CH_3)_2SO$ was cannulated into the flask, which was placed in an oil bath at 70 °C. Quinoxaline **7** was added as a solid in two portions, at *t* = 0 (0.0528 g) and *t* = 5 h (0.0252 g) for a total of 0.078 g (0.376 mmol, 2.02 equiv). The reaction mixture was stirred for 2 days. After cooling to 25 °C, the reaction solution was poured into 1 L of brine, and the mixture was extracted with CH_2Cl_2 (3 × 200 mL). The organic layer was repeatedly washed with H_2O and dried over $MgSO_4$. The solvent was evaporated under reduced pressure to give a brown semisolid. This was placed on a 2-mm-thick radial chromatography plate and eluted with CH_2Cl_2 and CH_2Cl_2/CH_3OH mixtures up to 10% CH_3OH. Only product **9** was isolated. The numerous other products were present in far too small amounts for characterization. There was isolated 0.0313 g (18%) of monoquinoxalinediol **9**: mp 157–158 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 0.90–1.03 (m, 12 H, $C_4H_8CH_3$), 1.22–1.52 (bm, 24 H, $CH_2C_3H_6CH_3$), 1.85 (bs, ~4 H, H_2O), 2.1–2.35 (bm, 8 H, $CH_2C_4H_9$), 2.60, 2.95 (s, impurities), 4.28–4.33 (overlapping doublets, buried triplet, 3 H, 2 H -OCH_iH_oO-, 1 H ArCH), 4.68 (t, *J* = 8.0 Hz, 1 H, ArCH), 4.71 (t, *J* = 8.0 Hz, 1 H, ArCH), 5.63 (d, *J* = 7.4 Hz, 1 H, -OCH_iH_oO-), 5.57–5.64 (doublet with triplet buried, *J* = 7.4 H, total of 2 H, 1 -OCH_iH_oO- and 1 ArCH), 5.73 (d, *J* = 7.4 Hz, 1 H, -OCH_iH_oO-), 6.27 (s, 1 H, ArH), 6.42 (s, 1 H, ArH), 7.07 (s, 1 H, ArH), 7.09 (s, 1 H, ArH), 7.16 (s, 1 H, ArH), 7.26 (s, 1 H, ArH), 7.264 (s, 1 H, ArH), 7.43 (s, 1 H, ArH), 7.78 (center of distorted AA′BB′ pattern, 4 H, ArH), 8.83 (bs, ~1 H, ArOH), 9.12 (bs, ~1 H, ArOH); MS (FAB, CH_2Cl_2) *m/e* 921 (M^+ + 3, 16), 920 (M^+ + 2, 57), 919 (M^+ + 1, 100), 918 (M^+, 44), 917 (M^+ – 1, 19). Anal. Calcd for $C_{58}H_{66}O_8N_2 \cdot CH_3OH$ (dried at 10^{-5} Torr, 80 °C, 10 h): C, 74.50; H, 7.42; N, 2.94. Found: C, 74.60; H, 7.79; N, 2.58.

2,12:3,11:40,50:41,49-Tetrametheno-4*H*,6*H*,8*H*,10*H*,-42*H*,44*H*,46*H*,48*H*-bis[1,3]dioxocino[5″,4″:8′,9′][1,3]benzodioxocino[5′,4′:8,9][1,3]benzodioxocino[5,4-*j*:5′,4′-*j*′]benzo-[1,2-*b*:5,4-*b*′]bis[1,4]benzodioxonin-26,52-dione, 4,6,8,10,42,44,46,48-Octapentyl- (Syn Stereoisomer C-10 and

(16) Perrin, D. D.; Armarengo, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1980.

Anti Stereoisomer Z-10). A solution of 0.2076 g (0.2578 mmol) of diol **4** in 16.3 mL of anhydrous $(CH_3)_2SO$ was flushed with argon for 20 min, and anhydrous Na_2CO_3 (1.09 g, 1.03 mmol) was added. The mixture was stirred under argon for an additional 10 min, and then fluoranil (**6**)[16] was added (a total of 29 mg, 0.161 mmol, 0.625 equiv) in five roughly equivalent portions at 90-min intervals. The first portion of fluoranil caused the nearly colorless sodium salt solution of the diol to turn dark brown. Over the course of fluoranil addition, a fine precipitate formed. The reaction was stirred an additional 2 days beyond fluoranil addition and then was added to 300 mL of distilled water which contained 10 mL of 2 N aqueous HCl. The mixture was stirred and filtered, and the brown residue was washed with several portions of distilled water. The residue was air-dried, dissolved in CH_2Cl_2, and subjected to radial chromatography (SiO_2, CH_2Cl_2). Alternatively, recrystallization of the crude residue from ethyl acetate provided most (~90%) of the **Z-10** present. The filtrate was evaporated, and the residue was dissolved in CH_2Cl_2 and subjected to radial chromatography to provide the remaining **Z-10** and all of the **C-10**. The **Z-10** was eluted first, followed by the **C-10**. Much dark polymeric material remained at the base line. The yield of bright yellow crystalline **Z-10** was 92.5 mg (0.054 mmol, 42%). The yield of beige-colored **C-10** was 26.4 mg (0.016 mmol, 12%). Single crystals of **Z-10** suitable for structure determination were obtained from a (pure) sample recrystallized from EtOAc and from $C_6H_5NO_2$; mp >360 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 0.903–0.944 (m, 12 H, $C_4H_8CH_3$), 1.25–1.41 (bm, 24 H, $CH_2C_3H_6CH_3$), 1.57 (H_2O), 2.15–2.35 (bm, 8 H, $CH_2C_3H_6CH_3$), 4.25 (d, J = 7.2 Hz, 2 H, -OCH_iH$_o$O-), 4.32 (d, J = 7.2 Hz, 4 H, -OCH_iH$_o$O-), 4.70 (t, J = 8.3 Hz, 2 H, Ar_2CH), 4.74 (t, J = 8.3 Hz, 4 H, Ar_2CH), 5.54 (t, J = 8.3 Hz, 2 H, Ar_2CH), 5.72 (d, J = 7.4 Hz, 2 H, -OCH$_i$H$_o$O-), 5.73 (d, J = 7.4 Hz, 4 H, -OCH$_i$H$_o$O-), 6.46 (s, 2 H, ArH), 7.14 (s, 2 H, ArH), 7.16 (s, 2 H, ArH), 7.18 (s, 2 H, ArH); UV-vis ($CHCl_3$) $c = 4.62 \times 10^{-5}$ M^{-1}, 25 °C, $A(\lambda_{max})$ = 240 nm, ϵ = 18 442 M^{-1} cm^{-1}, λ_{max} = 276 nm, ϵ = 17 649 M^{-1} cm^{-1}; MS (FAB, NOBA) m/e 1712 (cluster, M$^+$ + 3, 100). Anal. Calcd for $C_{108}H_{124}O_{18}$ (dried at 10^{-5} Torr, 80 °C, 24 h): C, 75.85; H, 7.31. Found: C, 75.66; H, 7.33.

Single crystals of **C-10** suitable for structure determination were grown from CH_3CN–CH_2Cl_2: mp >360 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 0.85–1.2 (m, 12 H, $C_4H_8CH_3$), 1.32–1.5 (bm, 24 H, $CH_2C_3H_6CH_3$), 1.55 (H_2O), 2.1–2.3 (bm, 8 H, $CH_2C_3H_6CH_3$), 4.27 (d, J = 7.2 Hz, 2 H, -OCH_iH$_o$O-), 4.34 (d, J = 7.2 Hz, 4 H, -OCH_iH$_o$O-), 4.69 (t, J = 8.2 Hz, 2 H, Ar_2CH), 4.74 (t, J = 8.0 Hz, 4 H, Ar_2CH), 5.16 (t, J = 8.2 Hz, 2 H, Ar_2CH), 5.29 (CH_2Cl_2) 5.72 (d, J = 7.4 Hz, 2 H, -OCH$_i$H$_o$O-), 5.74 (d, J = 7.4 Hz, 4 H, -OCH$_i$H$_o$O-), 6.43 (s, 2 H, ArH), 7.06 (s, 2 H, ArH), 7.11 (s, 4 H, ArH); UV-vis ($CHCl_3$) $c = 1.53 \times 10^{-5}$ M^{-1}, 25 °C, $A(\lambda_{max})$ = 240 nm, ϵ = 26 118 M^{-1} cm^{-1}, λ_{max} = 277 nm, ϵ = 19 494 M^{-1} cm^{-1}; MS (FAB, NOBA) m/e 1710 (cluster, M$^+$ + 1, 100); (field desorption +) 1709 (cluster, M$^+$, 100). Anal. Calcd for $C_{108}H_{124}O_{18}$ (dried at 10^{-5} Torr, 100 °C, 24 h): C, 75.85; H, 7.31. Found: C, 75.49; H, 7.43.

4,14:5,13:20,30:21,29-Tetrametheno-6*H*,8*H*,10*H*,12*H*,-22*H*,24*H*,26*H*,28*H*-[1,3]dioxocino[5‴,4‴:8″,9″][1,3]benzodioxocino[5″,4″:8′,9′][1,3]benzodioxocino[5′,4′:9,10][1,4-benzodioxonino[2,3-*b*][1,3]dioxocino[5⁗,4⁗:8‴,9‴][1,3]-benzodioxocino[5‴,4‴:9′,10′][1,4]benzodioxonino[2′,3′:5,6]-pyrazino[2,3-*g*]quinoxaline, 6,8,10,12,22,24,26,28-Octapentyl-(Stereoisomer Z-11). Diol **4** (0.169 g, 0.210 mmol) was dissolved in 14 mL of anhydrous $(CH_3)_2SO$ under an argon atmosphere. Anhydrous Na_2CO_3 was added and the reaction stirred for 15 min. Tetrachlorotetraazaanthracene (a total of 34 mg, 0.106 mmol) was added in four roughly equivalent portions at 2-h intervals. A TLC of the reaction mixture before addition of the second portion of tetrachlorotetraazaanthracene indicated that very little of the first portion had been consumed. The reaction flask was warmed to 60–70 °C with an oil bath and kept at that temperature for the remainder of the reaction. After all of the tetrachlorotetraazaanthracene had been added, the reaction mixture was stirred an additional 2 days. The flask was cooled to 25 °C, and the solution was added to 350 mL of water plus 10 mL of 2 N aqueous HCl. After stirring, the solution was filtered and the brown residue was washed with several portions of distilled water. The dried residue was dissolved in CH_2Cl_2 and subjected to radial chromatography using CH_2Cl_2/10% petroleum ether. The first fraction was isolated, fully characterized as a dimer product and tentatively assigned as the **Z-11** configuration by comparison of its chromatographic behavior with that of compounds **Z-10** and **C-10** (30.4 mg, 0.017 mmol, 16%). No other symmetrical compound was isolated. Isomer **Z-11** was characterized as follows: mp >360 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 0.937 (t, J = 6.6 Hz, 12 H, $C_4H_8CH_3$), 1.25–1.5 (bm, 24 H, $CH_2C_3H_6CH_3$), 1.56 (s, H_2O), 2.1–2.4 (bm, 8 H, $CH_2C_3H_6CH_3$), 4.23 (d, J = 7.2 Hz, 2 H, -OCH_iH$_o$O-), 4.28 (d, J = 7.4 Hz, 4 H, -OCH_iH$_o$O-), 4.67 (t, J = 8.2 Hz, 2 H, Ar_2CH), 4.74 (t, J = 8.2 Hz, 4 H, Ar_2CH), 5.63 (d, J = 7.4 Hz, 2 H, -OCH$_i$H$_o$O-), 5.69 (t, J = 8.2 Hz, 2 H, Ar_2CH), 5.73 (d, J = 7.4 Hz, 4 H, -OCH$_i$H$_o$O-), 6.40 (s, 2 H, ArH), 7.12 (s, 2 H, ArH), 7.20 (s, 2 H, ArH), 7.38 (s, 2 H, ArH), 8.60 (s, 2 H, ArH); MS (FAB, NOBA) m/e 1784 (M$^+$ + 1, 100). Anal. Calcd for $C_{112}H_{126}O_{16}N_4$ (dried at 10^{-5} Torr, 80 °C, 10 h): C, 75.40; H, 7.12; N, 3.14. Found: C, 75.34; H, 7.23; N, 2.98.

Crystal Structure Data. Compound **4**·H_2O·0.75$CHCl_3$ crystallized from $CHCl_3/H_2O$ as pale yellow parallelepipeds in the monoclinic system $P2_1/a$. Unit cell dimensions are as follows: a = 18.340 (2), b = 12.950 (1), and c = 22.165 (2) Å, β = 105.448 (3)°, V = 5074 Å^3, Z = 4. The crystal was examined on a modified Picker FACS-1 diffractometer, Mo K_α radiation, at 25 °C. The structure was determined by direct methods. Refinement of 318 + 44 parameters (2 blocks, of 9518 unique reflections, 3363 reflections with $I > 3\sigma(I)$) has an agreement value, R, currently at 0.080. There is also unidentified or disordered solvent in the region of the $CHCl_3$.

Compound **C-10**·3CH_3CN·CH_2Cl_2 crystallized from CH_2Cl_2/CH_3CN as yellow plates and parallelepipeds in the triclinic system $P\bar{1}$. Unit cell dimensions are as follows: a = 16.434 (2), 17.447 (2), and 19.888 (2) Å, α = 82.065 (3), β = 83.242 (3), and γ = 80.229 (3)°, V = 5540 Å^3, Z = 2. The crystal was examined on a modified Syntex P$\bar{1}$ diffractometer, Cu K_α radiation, at 25 °C. The structure was determined by direct methods. Refinement of 257 + 273 + 81 parameters (3 blocks, of 11395 unique reflections, 5068 reflections with $I > \sigma(I)$) has an agreement value, R, currently at 0.21. There is a molecule of CH_3CN in one bowl cavity and a molecule of CH_2Cl_2 in the other bowl cavity and CH_3CN in the region of the n-alkyl groups. Other solvent is interstitial and disordered.

Compound **Z-10**·4$CH_3COCH_2CH_3$ crystallized from $CH_3COC_2H_5/CH_3CN/C_2H_5OH$ as orange plates in the triclinic system $P\bar{1}$. Unit cell dimensions are as follows: a = 10.608 (1), b = 11.360 (1), and c = 23.909 (2) Å, α = 84.456 (3), β = 89.099 (3), and γ = 82.609 (3)°, V = 2844 Å^3, Z = 1 (the molecule is centrosymmetric). The crystal was examined on a Syntex P$\bar{1}$ diffractometer, Cu K_α radiation, at 25 °C. The structure was determined by direct methods. Refinement of 294 parameters (of 5855 unique reflections, 2074 reflections with $I > 3\sigma(I)$) has an agreement value, R, currently at 0.14. The solvent is disordered.

Compound **Z-10**·4$CH_3COOC_2H_5$ crystallized from $CH_3COOC_2H_5/CH_2Cl_2$ as yellow plates in the triclinic system $P\bar{1}$. Unit cell dimensions are as follows: a = 10.655 (3), b = 11.514 (3), and c = 23.914 (6) Å, α = 85.033 (8), β = 87.974 (7), and γ = 83.264 (8)°, V = 2882 Å^3, Z = 1 (the molecule is centrosymmetric). The crystal was examined on a Syntex P$\bar{1}$ diffractometer, Cu K_α radiation, at 25 °C. The structure was determined by direct methods. Refinement of 258 + 45 parameters (of 5980 unique reflections, 2665 reflections with $I > 3\sigma(I)$) has an agreement value, R, currently at 0.17. The solvent is disordered.

Compound **Z-10**·6$C_6H_5NO_2$ crystallized from $C_6H_5NO_2$ as yellow parallelepipeds in the triclinic system P$\bar{1}$. Unit cell dimensions are as follows: a = 12.548 (2), b = 12.742 (2), and c = 20.932 (3) Å, α = 90.628 (4), β = 104.657 (4), and γ = 93.028 (4)°, V = 3232 Å^3, Z = 1 (the molecule is centrosymmetric). The crystal was examined on a Huber diffractometer, Mo K_α radiation, at 25 °C. The structure was determined by direct methods. Refinement of 265 + 73 parameters (of 8466 unique reflections, 1753 reflections with $I > 3\sigma(I)$) has an agreement value, R, currently at 0.128.

Further crystallographic details will be published elsewhere.