290 (M^+, 2.47), 275 (17.32), 257 (9.10), 205 (5.42), 192 (14.74), 177 (29.12), 163 (7.85), 149 (24.61), 137 (55.40), 123 (38.29), 109 (47.97), 95 (65.33), 81 (84.99), 69 (81.83), 55 (62.59), 41 (100.00); HREIMS calcd for $C_{20}H_{34}O$ (M^+) 290.2609, found 290.2613.

(+)-Labda-8(17),13(*E*)-dien-15-ol (copalol, 39): yield 27.2 mg (92%) as a colorless oil. The IR, ^1H NMR, ^{13}C NMR ($\Delta\delta \leq 0.07$ ppm), and mass spectra of (+)-**39** are identical to those of *ent*-copalol ((−)-**39**). Data for (+)-**39**: $[\alpha]^{24}_D$ +29.8° (*c* 1.36, $CHCl_3$) (lit.[58] $[\alpha]_D$ +30° (*c* 1.09, $CHCl_3$)); IR (neat) 3300, 2922, 1643, 1442, 1387. 997, 887 cm^{-1}; ^1H and ^{13}C NMR data (see Table I); MS (70 eV) *m/e* (relative intensity) 290 (M^+, 2.97), 275 (19.22), 257 (10.31), 205 (6.86), 191 (12.58), 177 (13.19), 161 (7.04), 149 (18.34), 137 (71.78), 123 (44.58), 109 (50.21), 95 (73.41), 81 (95.38), 69 (83.81), 55 (71.14), 41 (100.00); HREIMS calcd for $C_{20}H_{34}O$ (M^+) 290.2609, found 290.2613.

(−)-Labda-8(17),13(*E*)-dien-15-ol (*ent*-39). The reference sample of naturally derived *ent*-copalol was obtained by AlH_3 reduction of methyl copalate. The ester was prepared by CH_2N_2 esterification of copalic acid isolated from Brazilian copal resin.[48,59] They are identical with those for synthetic (+)-**39**.

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Supplementary Material Available: Spectral data for triethyl 2-[(trimethylsilyl)methyl]-2-phosphonobutanoate, procedures for preparation of the ester precursor to **17** (method B), logic used to assign NMR data for **5**, ^1H NMR spectra for **14b**, **18a**, **18c**, **27a**, **28a**, **28c**, **35–39**, **5**, and **6**, and ^{13}C NMR, COSY, and HETCOR spectra of **5** and **39** (25 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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Cavitands as Versatile Molecular Receptors

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X-ray crystal structure of **3**·2PhF and ^1H NMR complexation studies in solution reveal the strong tendency of cavitand **3** to selectively bind aromatic guests in organic solution. The association constants (K_a) for eight 1:1 caviplexes formed in acetone-d_6 were determined. The solvation effect is largely responsible for the relatively low K_a values observed. The orientation assumed by the guests inside the cavity is determined by dipole–dipole interactions between the host and the guest; additional CH_3–π interactions are present in the case of **3**·3$(CH_3)_2CO$. The modification of the structure of **3** by introducing a suitable and furtherly modifiable substituent allowed the synsesis of optically pure chiral cavitand **5**. ^1H NMR complexation studies of **5** in acetone-d_6 reveal that the CH_2OH group perching on top of the cavity rim affects the selectivity but not the orientation of the included aromatic guests for the 1:1 caviplexes formed.

The design of new molecular receptors, combining binding and orientation of neutral guests, requires the comprehension and modulation of the weak attractive forces responsible for molecular recognition phenomena.[1] Chirality and the presence of convergent functional groups are two further desirable features.

Among others, cavitands, synthetic organic compounds with enforced concave surfaces of molecular dimensions,[2] are extremely interesting and versatile synthetic receptors. Some attractive features of cavitands have been previously reported: the presence of a tunable solvation-temperature-driven equilibrium between a closed vaselike and an open kitelike form[3] and their strong tendency to complex organic molecules in the solid state,[4] in solution,[5] and in the gas phase,[6] with preference for aromatic guests.

In this paper we report the X-ray crystal structure of **3**·2PhF, the synthesis of chiral cavitands **4** and **5** (Scheme I), and the complexation studies in organic solution of **3** and **5** with aromatic guests.

Results and Discussion

Crystal Structure of 3·2PhF. The crystal and molecular structure of **3**·2PhF was determined by single-crystal X-ray diffraction methods. As shown in Figure 1, the conformation of the host molecule resembles that observed in the previously reported **3**·3$(CH_3)_2CO$[5] and in the analogue **6**·2CH_2Cl_2[3] (Scheme I). A deep intramolecular

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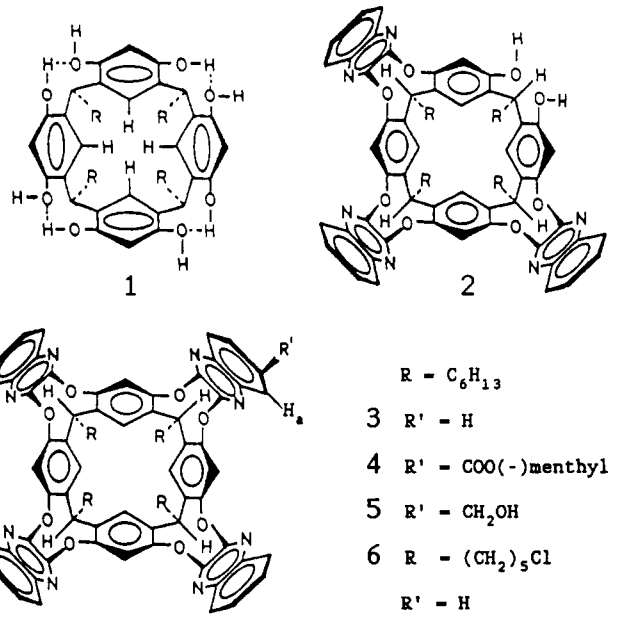
Table I. Torsion Angles Involving the Aliphatic Chains in 3•2PhF and 3•3$(CH_3)_2CO$

	3·2PhF				3·3$(CH_3)_2CO$			
	A	B	C	D	A	B	C	D
C18–C19–C20–C21	167.6 (8)	−166.1 (8)	−56 (1)	65 (1)	165 (1)	7 (1)	−180 (1)	66 (1)
C19–C20–C21–C22	−175.4 (7)	−162 (2)	173.0 (7)	−163.2 (7)	175 (1)	153 (2)	179 (1)	−177 (1)
C20–C21–C22–C23	−160.4 (7)	−66 (1)	156.2 (8)	−107.7 (8)	−178 (1)	129 (3)	178 (2)	−65 (3)
C21–C22–C23–C24	159.2 (7)	165 (1)	179.3 (7)	172.8 (8)	−174 (1)	−168 (4)	−169 (3)	175 (2)
C22–C23–C24–C25	158.6 (8)	76 (1)	−126.4 (9)	105 (1)	−130 (2)	55 (9)	−44 (4)	51 (3)

Scheme I



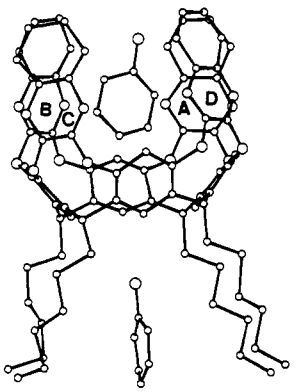


Figure 1. X-ray molecular structure of 3·2PhF, side view.

cavity, in the vase conformation, is created by the four quinoxaline groups, making the host molecule highly preorganized toward complexation of small neutral guests.

The conformation of the cavity can be described by the dihedral angles between the least-squares planes through the quinoxalines and the least-squares plane (taken as reference plane) through the C bridges which support the aliphatic chains: 86.8 (2), 80.2 (2), 85.6 (2), 77.1 (2)°. These values are quite close to those observed in the 3·3$(CH_3)_2CO$ derivative: 87.8 (2), 80.6 (2), 89.8 (2), 79.8 (2)°. The first fluorobenzene guest molecule fills the intramolecular cavity with the C–F axis inclined 19.2 (2)° with respect to the normal to the reference plane and points the F atom toward the portal of the vase. The dihedral angles between the least-squares planes through the four quinoxaline groups (A–D) and the fluorobenzene plane are as follows: 176 (3), 21.6 (3), 124.6 (3), and 25.0 (3)°, respectively (Figure 2). These values are significantly different from those observed in 3·3$(CH_3)_2CO$, where the first acetone molecule is blocked by an attractive CH_3-π interaction

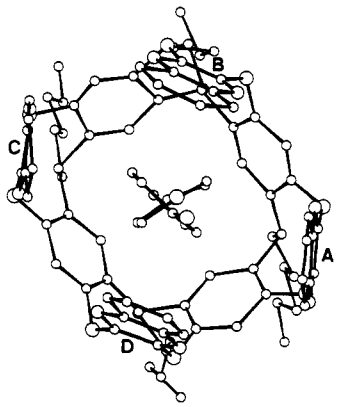


Figure 2. X-ray molecular structure of 3·2PhF, end view.

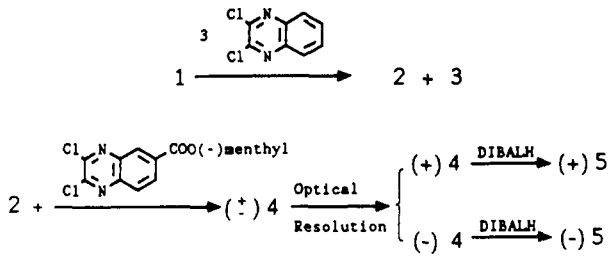
which orients the averaged plane through acetone to form dihedral angles of 48.2 (2), 51.9 (2), 48.7 (2), and 57.0 (2)°. The electric dipole vector of the guest is at ca. 160° with the dipole vector of the host cavity. Such reciprocal orientation between host and guest dipole vectors has been already observed in 6·2CH_2Cl_2 and in 3·3$(CH_3)_2CO$, where the guests inside the vase orient their dipole moments opposite to that of the host. The intermolecular host–fluorobenzene distances in the vase cavity are consistent with van der Waals interactions.

A second fluorobenzene guest molecule is included in the apolar niche created by the four aliphatic chains on the bottom of 3, with the C–F axis tilted 7.1 (6)° with respect to the normal to the reference plane. The dihedral angle between the least-squares planes of the two fluorobenzene molecules is 73.6 (2)°. The second fluorobenzene is blocked by the intermolecular hydrogen bond C–H···F (C20A–H20A, 1.08 Å, C20A···F1G, 3.33 (1) Å, and the C–H···F angle of 147.8 (4)°). However, as shown by the torsion angles reported in Table I, the shape of the niche created by the aliphatic chains in 3·2PhF is quite different from that observed in the 3·3$(CH_3)_2CO$ complex, in which the shortest intermolecular $O_{acetone}$–C_{chain} contact between the oxygen atom of the second acetone molecule and the C(20) atoms of the aliphatic chains is 3.62 (1) Å. So in 3·$(CH_3)_2CO$ the presence of any intermolecular hydrogen bond may be excluded.

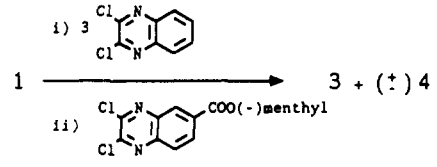
On the other hand, the calculated density of 3·2PhF is 1.30 g cm^{-3} whereas for 3·3$(CH_3)_2CO$ is 1.21 g cm^{-3}; thus, the difference is more significant than the low gain in mass (1521.81 amu versus 1503.84 amu). In the absence of any significant change of the geometry of the vase cavity, the increase of the density in the presence of an aromatic guest may be ascribed to a more efficient packing mode of the aliphatic chains, probably driven by the hydrogen bond already described.

Synthesis of Chiral Cavitands 4 and 5. The synthetic approach is shown in Scheme II. The chosen strategy was to modify the structure of 3 by introducing an appropriate substituent on the upper rim of the cavity in such a way that the resulting cavitand becomes planary chiral and bears a functional group perching on top of the cavity. The (−)-menthyl carboxylic ester moiety was the resolving agent

Scheme II



Scheme III



of choice because it proved to be stable under the reaction conditions employed and it led to the formation of two separable diastereoisomers, (+)- and (−)-4. The first step was the synthesis of the cleft-shaped cavitand 2. Reaction of macrocyclic octol 1[7] with 3 equiv of 2,3-dichloroquinoxaline afforded 2 (53%) and 3 (27%). Cleft-shaped 2 is a white solid, slightly unstable to light and well-soluble in most common organic solvents. The next step was the reaction of 2 with 2,3-dichloro-6-quinoxaline carboxylic acid (−)-menthyl ester. The presence of a chiral auxiliary led to the formation of a separable mixture of the two diastereoisomers (+)- and (−)-4, which were isolated by silica gel chromatography. Their optical purity was checked by ^{1}H NMR analysis: in $CDCl_3$ the H_a doublet chemical shift is 8.65 ppm for (+)-4 and 8.62 ppm for (−)-4. Chiral cavitand 4 was alternatively obtained via a one-pot procedure (Scheme III) reacting 1 first with 3 equiv of 2,3-dichloroquinoxaline and then with 1 equiv of 2,3-dichloro-6-quinoxalinecarboxylic acid (−)-menthyl ester. Removal of the chiral auxiliary was achieved by reducing the menthyl ester with DIBALH: (+)-4 gave the dextrorotatory alcohol, (+)-5, and (−)-4 the levorotatory one, (−)-5.

Complexation Properties of Cavitand 3. Cavitand 3 selectively binds aromatic compounds in organic solvents.[5] In acetone, 1:1 caviplexes precipitated when the guest concentration reached a critical value (usually three to five times the host concentration). The solids were isolated and dried untill constant weight. ^{1}H NMR, thermogravimetric, and elemental analyses evidenced the 1:1 stoichiometry of the isolated caviplexes.[4] ^{1}H NMR titration of aromatic guests in acetone-d_6 with cavitand 3 allowed the determination of the association constants (K_a) for eight 1:1 caviplexes formed (Table II).[8] For nitrobenzene and 4-nitrotoluene a quantitative evaluation of K_a was impossible due to overlap of the signals of the host and the guest. No complexation was observed with 4-fluorobenzaldehyde and 2-fluorotoluene. The low K_a values observed can be attributed to competition for the lipophilic cavity between the solvent (acetone) and the guests. In fact, no association was detected for the same guests by switching to a more lipophilic solvent like $CDCl_3$.

During the evaluation of ^{1}H NMR data we observed that in two cases (runs 3 and 8, Table II) the orientation of the guests inside the cavity could be determined. The large upfield shift and the shape broadening of the proton signals ortho to the NMe_2 group with respect to the meta ones (Figure 3) indicate that the orientation of the NMe_2 group inside the cavity is preferred. This is in accordance both with the presence of CH_3-π interaction between the quinoxalines and the methyl groups and with the dipole–dipole interactions between host and guest.[9]

Table II. ^{1}H NMR Association Constants (K_a) and Free Energies of Complexation ($\Delta G°$) for the 1:1 Complexes 3•Guest in Acetone-d_6, at T = 298 K

run	guest X	guest Y	K_a (M^{-1})	$-\Delta G°$ (kcal mol^{-1})
1	Cl	H	29	2.0
2	F	H	48	2.3[a]
3	NMe_2	CN	48	2.3
4	NCO	H	57	2.4
5	H	H	66	2.5
6	CH_3	H	86	2.6
7	NCO	CH_3	105	2.8
8	NMe_2	NO_2	200	3.1

[a] More accurate calculations determined a lower K_a value than the previously reported one.[5]

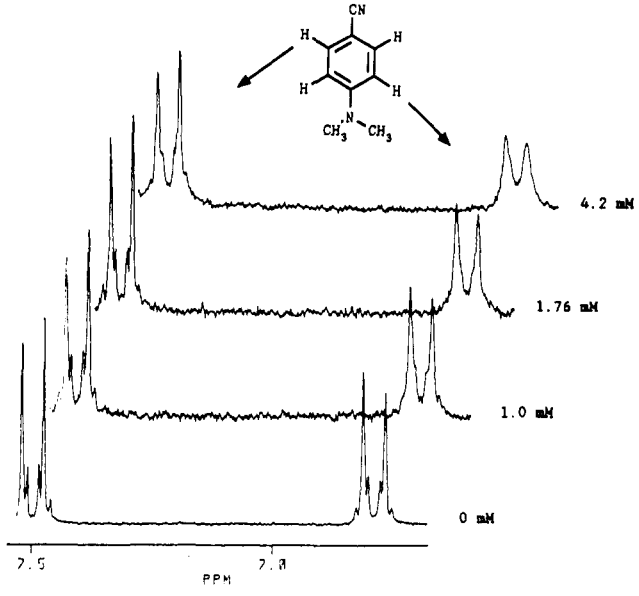


Figure 3.

The structural changes introduced in the parent molecule have a great influence on the molecular properties of cavitands. Also cavitands 4 and 5, as already reported for 3, form 1:1 caviplexes in the solid state. Thermogravimetric analyses of 4•C_6H_{14} and 5•$(CH_3)_2CO$ indicate that both guests are tightly included in the host cavity: in the first case *n*-hexane is released at 110 °C, while in the second one acetone is lost at 118 °C, temperatures well above the boiling points of the guest component. Cavitand 5 binds 4-(dimethylamino)benzonitrile and 4-(dimethylamino)-nitrobenzene in acetone-d_6 solution with K_a values, respectively, of 196 and 48 M^{-1} (^{1}H NMR titration), the opposite trend with respect to 3 (see runs 3 and 8, Table II). As already discussed for 3, the upfield shift variation and shape broadening of the proton signals ortho to the NMe_2 group indicate the preferred orientation of the guests with the NMe_2 group inside the cavity. The CH_2OH group on the rim of the cavity affects the selectivity but not the orientation of the complexed aromatic guests.

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(8) Saturation binding of 3 in benzene solution using time-resolved fluorescence furtherly confirmed the 1:1 caviplex stoichiometry.

(9) Preliminary force field calculations indicated for 3 in the C_{4v}-vase conformation a dipole moment of 3.2 D.

Conclusions

Analysis and comparison of **3**·2PhF, **3**·3$(CH_3)_2CO$, and **6**·2CH_2Cl_2 indicate the presence of two kinds of interactions between host and guest in the solid state, besides van der Waals interactions. The orientation assumed by fluorobenzene, acetone, and methylene chloride in the cavity is dictated by dipole–dipole interactions between host and guest. In the case of **3**·3$(CH_3)_2CO$ additional CH_3–π interactions between the hydrogen atoms of the methyl groups and the π electrons of two quinoxalines are present. Both interactions seems to play a role also in the complexation of aromatic molecules in acetone solution by **3** and **5**. In this case, however, solvation effects are dominant: the relatively low K_a values obtained can be attributed to the competition for the cavity space between the solvent and the guest. In fact, almost any solvent can enter and solvate the large, open-top vaselike cavity of both **3** and **5**. Higher K_a values could be obtained either by switching to more polar solvents[10] or by narrowing the cavity entrance.

Two other interesting features of **3** require mention: the shape of the preorganized cavity and the molecular packing in the crystal are independent from the included guest. Besides, both **3** and **6** crystallize in noncentrosymmetric space groups (C_c for **3** and $P4_12_12$ for **6**). Due to these interesting properties, inclusion of molecules having large second-order microscopic polarizability like nitroanilines into cavitands like **3** and **6** could generate acentric nonlinear optical materials.[11]

The synthesis of optically pure cavitand **5**, easily modifiable with suitable functional groups, opens up the way toward a new class of versatile molecular receptors, useful in the areas of catalysis, transport, separation technology, and molecular electronics.

Experimental Section

General. ACS-grade reagents were used without further purification. THF was distilled under nitrogen from sodium benzophenone ketyl. DMSO was dried over 3-Å molecular sieves. Commercial 2,3-dichloroquinoxaline was recrystallized from methanol before use. ^1H NMR spectra were recorded with a 200-MHz spectrometer. Either EI or desorption chemical ionization (DCI) mass spectrometry was used according to the kind of compound. Melting points are uncorrected. Silica gel 60 (230–400 mesh) was used for column chromatography. TLC was performed on Merck silica gel 60 F 254 precoated plates. Elemental analyses were performed by the microanalytical laboratory of the Donegani Institute.

^1H NMR Titrations. All ^1H NMR experiments were run at 298 K. In each titration the total guest concentration was kept constant. When possible, the host and guest concentrations were chosen to vary the percentage of guest complexation from about 10 to 40%.[12] Stock solutions of host and guest in acetone-d_6 were prepared, and desired concentrations were achieved by pipetting appropriate amounts of each stock solution and of pure solvent. Guest concentration was 2×10^{-3} M, and host concentrations varied from 0.5×10^{-3} to 5×10^{-3} M. The K_a of the 1:1 caviplexes formed were determined from the titration curves by using a computer-assisted nonlinear least-squares curve-fitting procedure.[13]

Crystal Structure Data on 3·2PhF. Compound 3·2PhF crystallizes from fluorobenzene as colorless monoclinic crystals: $C_{84}H_{80}N_8O_8 \cdot 2C_6H_5F$; M = 1521.813 amu; monoclinic a = 19.070 (3) Å, b = 17.916 (3) Å, c = 23.934 (3) Å, β = 108.96 (3)°; space group C_c; Z = 4; $F(000)$ = 3216; D_{calc} = 1.307 g cm^{-3}; μ(Cu K_α) = 6.63 cm^{-1}.

X-ray measurements were performed at room temperature on a Siemens A.E.D. 3-circles diffractometer using Ni-filtered Cu K_α radiation at λ = 1.541 78 Å. The cell parameters were determined by least-squares fit of 36 $(\theta,\chi,\phi)_{hkl}$ reflections found in a random search on the reciprocal lattice in the range $3l \le \theta \le 45°$. The systematic data collection was extended from $\theta \ge 3$ to $\theta \le 70°$ using a scan width from $[\theta - 0.65]°$ to $[\theta + 0.65 + \Delta\lambda \cdot \lambda^{-1} tg\theta]°$. Crystal stability and instrumental linearity were monitored by the measurements of one standard reflection every 100 collected reflections. No significant changes were observed either in the intensity or in the crystal orientation. The intensities were determined by profile analysis according to the Lehmann and Larsen procedure[14] and corrected for Lorentz and polarization effects. No corrections were made for absorption effects.

A total of 8113 reflections $\pm h, +k, +l$ ($h + k + l$ with $h + k = 2n$) were measured. The 3880 having $I > 3\sigma(I)$ were retained as observed and used in the structure refinement. The structure was solved by Direct Methods using the SHELX86[15] and refined with the SHELX76[16] package of crystallographic computer programs.

The atomic numbering scheme adopted for the host molecule is consistent with that of **3**·3$(CH_3)_2CO$ published elsewhere.[5] Each of the aliphatic chains showed a disorder which was impossible to fit in two different orientations. They were refined with some geometrical constraints on the C–C bonds and C–C–C angles.

The structure was refined with blocked full-matrix least-squares to a total of 806 (403 + 403) parameters. Parameters refined were the overall scale factor, the atomic coordinates, and the anisotropic thermal parameters for all the atoms with the exception of the C atoms of the alphatic chains and the two guest molecules. The H atoms were introduced in their calculated position with the geometrical constraint C–H = 1.08 Å and refined "riding" on the corresponding C atoms.

Due to the disorder only the H atoms bonded to the first atoms of the aliphatic chains (C20) were included. The refinement was stopped at R = 0.0697, R_w = 0.0516, $W = (\sigma(Fo))^{-2}$. The height of the maximum peak in the final Fourier ΔF map was 0.18 e·Å^{-3}. The geometrical calculations were performed by PARST.[17] The atomic scattering factors were obtained by analytical approximation according to the literature.[18] The calculations were carried out on the GOULD Encore 91 of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy.

2,3-Dichloro-6-quinoxalinecarboxylic Acid (–)-Menthyl Ester. 2,3-Dichloro-6-quinoxalinecarbonyl chloride[19] (13.5 g, 51.7 mmol) and (–)-menthol (8.1 g, 51.8 mmol) were refluxed 15 h in 500 mL of toluene. The dark-gray heterogeneous solution was cooled to room temperature, quenched with an aqueous Na_2CO_3 solution, extracted with diethyl ether (4 × 150 mL), and dried over Na_2SO_4. Purification by silica gel chromatography (petroleum ether 40–70 °C/EtOAc (7:3)) followed by crystallization from diethyl ether/methanol (1:1) afforded 14.8 g (75%) of pure product: colorless solid; mp 129–130 °C; $[\alpha]^{20}_D$ –6.03 (*c* 1.3, $CHCl_3$); EI MS *m/z* (relative intensity) 380 (8, M), 225 (35, M – menthoxy), 197 (18, M – COOmenthyl); IR (neat) ν 1714 cm^{-1} (C=O); ^1H NMR δ 8.68 (d, J = 1.7 Hz, 1 H, ArH), 8.38 (dd, J_1 = 8.7 Hz, J_2 = 4.4 Hz, 1 H, ArH), 8.04 (d, J = 8.7 Hz, 1 H, ArH), 4.97 (td, J_1 = 10.5 Hz, J_2 = 4.4 Hz, 1 H, OCH), 2.25–0.95 (m, 9 H, menthyl-H). Anal. Calcd for $C_{19}H_{22}Cl_2N_2O_2$: C, 59.85; H, 5.81; N, 7.35; Cl, 18.60. Found: C, 59.87; H, 5.85; N, 7.29; Cl, 18.55.

***r*-11,*c*-13,*c*-15,*c*-40-Tetrahexyl-9,17-methano-11*H*,13*H*,15*H*-bisbenzo[5′,6′]quinoxalino[2″,3″:2′,3′][1,4]benzodioxonino[10′,9′:5,6:9″,10″:8,9][1,4]dioxonino[2,3-*b*]-**

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quinoxaline-8,18-diol (2). Octol 1 (6.9 g, 11.7 mmol), 2,3-dichloroquinoxaline (7.0 g, 35.0 mmol), and K_2CO_3 (6.45 g, 46.7 mmol) in 150 mL of DMSO were stirred 8 h at rt and then 18 h at 50 °C. After the mixture was cooled to rt, 300 mL of water were added and the crude solid formed was filtered, washed with water (500 mL), and dried under reduced pressure. Purification by silica gel chromatography (CCl_4/EtOAc (85:15)) afforded cavitand **3** (4.3 g, 27%, R_f = 0.55) and the pure product **2** as a white solid (7.5 g, 53%, R_f = 0.25): mp 189–191 °C; DCI MS (isobutane) m/z 1202 ([M]$^{\bullet-}$); ^{1}H NMR ($CDCl_3$) δ 8.74 (bs, 2 H, OH), 8.22 (s, 2 H, ArH octol), 7.95–7.82 (m, 4 H, ArH), 7.66–7.29 (m, 10 H, ArH quinoxaline), 7.15 (s, 2 H, ArH octol), 7.12 (s, 2 H, ArH octol), 5.60–5.35 (m, 3 H, Ar*CH*), 4.34 (t, J = 7.1 Hz, 1 H, Ar*CH*), 2.45–2.05 (m, 8 H, CH*CH*$_2$), 1.60–1.10 (m, 32 H, CH_2), 0.92 (t, J = 6.1 Hz, 12 H, CH_3). Anal. Calcd for $C_{76}H_{78}N_6O_8$: C, 75.85; H, 6.53; N, 6.98. Found: C, 75.77; H, 6.61; N, 6.72.

(+)- and (−)-3-Carbo(−)menthoxy-*r*-9,*c*-11,*c*-13,*c*-15-tetrahexyl-7,17:8,16-dimetheno-9*H*,11*H*,13*H*,15*H*-quinoxalino[2‴,3‴:2‴,3‴][1,4]benzodioxonino[10‴,9‴:5,6]quinoxalino[2′,3′:2′,3′]quinoxalino[2″,3″:2″,3″][1,4]dioxonino[6″,5″:9′,10′][1,4]benzodioxonino[6′,5′:9,10][1,4]benzodioxonino[2,3-*b*]quinoxaline ((+)-4 and (−)-4). Cavitand **2** (6.2 g, 5.1 mmol), 2,3-dichloro-6-quinoxalinecarboxylic acid (−)-menthyl ester (1.9 g, 5.1 mmol), and K_2CO_3 (0.9 g, 6.5 mmol) were stirred 24 h at 50 °C in 75 mL of DMSO. After the mixture was cooled to rt, 150 mL of water was added. The crude precipitate was filtered, washed with water (200 mL), and dried under reduced pressure at 80 °C. *n*-Hexane (250 mL) was added and the solution refluxed 15 min and then filtered to remove some unreacted starting materials. Crystallization from the organic solution gave the pure product (5.9 g, 76%) as a colorless solid racemic mixture. The two diastereoisomers were separated through silica gel chromatography (*n*-hexane/EtOAc (9:1)). Before characterization the products were carefully dried (3 h, 130 °C (0.1 mmHg)). (+)-4: R_f = 0.28; mp 166–168 °C; $[\alpha]^{20}_D$ +9.0 (*c* 1.0, $CHCl_3$). (−)-4: R_f = 0.20; mp 153–155 °C; $[\alpha]^{20}_D$ −9.5 (*c* 1.0, $CHCl_3$); DCI MS (isobutane) m/z 1510 ([M]$^{\bullet-}$); IR (neat) ν 1717 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 8.65 (+)-4 and 8.62 (−)-4(d, J = 1.7 Hz, 1 H, H_a), 8.14 (m, 4 H, ArH octol), 8.09 (dd, J_1 = 8.7 Hz, J_2 = 1.8 Hz, 1 H, H_b), 7.85–7.70 (m, 7 H, ArH quinoxaline), 7.54–7.45 (m, 4 H, ArH quinoxaline), 7.40–7.35 (m, 2 H, Ar-H quinoxaline), 7.23–7.18 (m, 4 H, ArH octol), 5.60–5.40 (m, 4 H, Ar*CH*), 5.06 (td, J_1 = 10.8 Hz, J_2 = 4.2 Hz, 1 H, *CH*O), 2.34–2.15 (m, 8 H, ArCH*CH*$_2$), 2.10–1.12 (m, 41 H, CH and CH_2), 1.08–0.77 (m, 21 H, CH_3). Anal. Calcd for $C_{95}H_{98}N_8O_{10}$: C, 75.47; H, 6.53; N, 7.41. Found: C, 75.50; H, 6.58; N, 7.46.

Cavitands (±)-4 (One-Pot Procedure). Octol 1 (6.9 g, 11.7 mmol), 2,3-dichloroquinoxaline (7.0 g, 35.0 mmol), and K_2CO_3 (6.45 g, 46.7 mmol) in 150 mL of DMSO were stirred at rt for 8 h and successively 18 h at 50 °C. 2,3-Dichloro-6-quinoxalinecarboxylic acid (−)-menthyl ester (2.5 g, 6.6 mmol) and K_2CO_3 (0.9 g, 6.5 mmol) were then added and the resulting solution further heated for 24 h. After the mixture was cooled to rt, 150 mL of water were added. The crude precipitate was filtered, washed with water (400 mL), and dried under reduced pressure at 80 °C. Purification by silica gel chromatography (*n*-hexane/EtOAc (9:1)) afforded 4.2 g (27%) of cavitand **3** (R_f = 0.10), 3.1 g of (+)-4 (R_f = 0.28), 2.2 g of (−)-4 (R_f = 0.20), and 1.9 g of a (+)-4 and (−)-4 mixture (41% overall yield of 4).

(+)-3-(Hydroxymethyl)-*r*-9,*c*-11,*c*-13,*c*-15-tetrahexyl-7,17:8,16-dimetheno-9*H*,11*H*,13*H*,15*H*-quinoxalino[2‴,3‴:2‴,3‴][1,4]benzodioxonino[10‴,9‴:5,6]quinoxalino[2′,3′:2′3′]quinoxalino[2″,3″:2″,3″][1,4]dioxonino[6″,5″:9′,10′][1,4]benzodioxonino[6′,5′:9,10][1,4]benzodioxonino[2,3-*b*]quinoxaline (+)-5. A solution of cavitand (+)-4 (2.0 g, 1.3 mmol) in dry THF (50 mL) was added dropwise over 30 min to a solution of DIBALH (6 mL of a 1 M solution in THF) in 50 mL of dry THF under a nitrogen purge. The resulting solution was stirred 2 h at rt and then cooled to 0 °C and carefully quenched with a saturated aqueous solution of NH_4Cl and finally extracted with diethyl ether (3 × 100 mL). After drying (Na_2SO_4), the solvent was removed under reduced pressure and the residue chromatographed over silica gel (n-hexane/EtOAc 2:8) giving pure (+)-5 (1.7 g, 95%). Before characterization the products were carefully dried (3 h, 130 °C (0.1 mHg)): mp 206–207 °C; $[\alpha]^{20}_D$ +4.6 (*c* 1.0, $CHCl_3$); DCI MS (isobutane) m/z 1358 ([M]$^{\bullet-}$); ^{1}H NMR ($CDCl_3$) δ 8.17–8.14 (m, 4 H, ArH octol), 7.83–7.69 (m, 8 H, Ar-H quinoxaline), 7.51–7.42 (m, 7 H, ArH quinoxaline), 7.24–7.20 (m, 4 H, ArH octol), 5.57 (t, J = 7.9 Hz, 4 H, Ar*CH*), 4.81 (s, 2 H, *CH*$_2$OH), 2.31–2.23 (m, 8 H, CH*CH*$_2$), 1.6–1.2 (m, 32 H, CH_2), 0.93 (t, J = 6.4 Hz, 12 H, CH_3). Anal. Calcd for $C_{85}H_{82}N_8O_9$: C, 75.09; H, 6.08; N, 8.24. Found: C, 75.09; H, 6.10; N, 8.20.

Cavitand (−)-5. The same procedure employed for (+)-5 gave 1.7 g (95%) of pure (−)-5: mp 206–207 °C; $[\alpha]^{20}_D$ −4.6 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{85}H_{82}N_8O_9$: C, 75.09; H, 6.08; N, 8.24. Found: C, 75.12; H, 6.10; N, 8.23.

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Supplementary Material Available: Tables of final atomic coordinates, thermal parameters, bond distances, bond angles, and torsion angles (22 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Palladium-Mediated Arylation of Acetylated Enones Derived from Glycals. 4.† Synthesis of Aryl 2-Deoxy-β-D-*C*-glycopyranosides

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The palladium-mediated arylation of the peracetylated glycal-derived enones **1**, **2**, and **3** afforded mixtures of *C*-glycosides containing an arylated enone (**1a**, **2a**, or **3a**) and an arylated ketone (**1b**, **2b**, or **3b**). A rationale for the formation of these compounds is given. Reduction of the arylated enones proceeds in a stereospecific manner, thus affording aryl 2-deoxy-β-D-C-glycopyranosides in high yield.

The formation of a C–C bond at the anomeric center of a carbohydrate has become an increasingly important area of study in synthetic organic chemistry since a wide variety of *C*-glycosides have been isolated from natural sources.[1] Among them, aryl *C*-glycosides are of particular interest due to their antibiotic and antitumor activity.[1] Several

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