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Stoichiometric Inclusion Compounds of Cyclotriveratrylene and Cyclotricatechylene with Small Neutral Molecules. X-ray Crystal Structure of Cyclotricatechylene Di-2-propanolate

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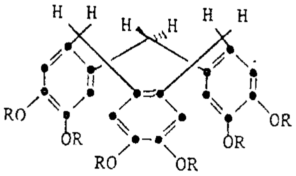
Guest–host complexes of a number of small organic molecules with cyclotriveratrylene (**1a**) and cyclotricatechylene (**1b**) have been prepared and characterized by IR and NMR spectroscopy. The crystal structure of the 1:2 **1b**–2-propanol complex has been determined. The crystals are in the space group $P\bar{1}$ with a = 9.605 (2), b = 9.819 (2), c = 13.737 (3) Å, α = 95.36 (2), β = 94.30 (2), γ = 99.54 (2)°, and there are two molecules in the unit cell. The structure was refined to an R factor of 0.075 on 3448 nonzero reflections. The molecules of **1b** adopt a "crown" conformation in the crystal but the disposition and hydrogen-bonding patterns of the hydroxyl groups destroy threefold symmetry. The **1b** molecules form a channel held together by hydrogen bonds although there are constrictions which serve to prevent translational motion of the guest 2-propanol molecules. Each 2-propanol molecule acts as a donor and an acceptor in a hydrogen bond to **1b** molecules.

The formation of crystalline solids in which a small molecule is incorporated in a regular way into the structure of a larger one has been a subject of considerable interest for many years.[1] Complexes of this type may have great stability and there has been interest in classifying such structures as clathrates (in which one component forms cages imprisoning the other) or channel complexes. Such complexes have been of value in separations (including optical resolutions) as well as having possible interest from the point of view of changing reactivity of the guest molecules by virtue of imposing specific restrictions.

The compound cyclotriveratrylene (**1a**) is of particular interest because of its ready availability and reported[2] formation of inclusion compounds. Its demethylated derivative **1b** (10,15-dihydro-2,3,7,8,12,13-hexahydroxy-5*H*-tribenzo[*a*,*d*,*g*]cyclononene), for which we propose the name cyclotricatechylene,[5] was found during the course of a synthetic investigation[6] to be still more prone to complex formation than is the methyl ether **1a**. In addition, the complexes of **1b** are better defined than those of **1a**. This paper reports a survey of the complexes of **1b** and the X-ray crystal structure determination of the complex of **1b** with 2-propanol.



1a, R = CH_3

1b, R = H

Experimental Section[7]

Cyclotricatechylene (1b) was prepared as described earlier[6] and dried in vacuum at 70 °C for 24 h after ethanol–water recrystallization (Norit). The material was found to be free of water and solvent by IR and NMR analyses.

Table I. Cyclotricatechylene (1b) Inclusion Compounds[a]

guest molecule	complex[b]	ratio 1b: guest[c]
N,*N*-dimethylformamide	yes	1:3.1
N-methylpyrolidinone	yes	1:3.0
N,*N*-dimethylacetamide	yes	1:3.1
dimethyl sulfoxide	yes	1:3.0
water	yes[d]	1:3.0
hexamethylphosphoric triamide	yes	1:3.0
acetone	yes	1:2.0
2-propanol	yes	1:2.0
ethanol	no	
methyl isobutyl ketone	no	

[a] See experimental section for method of preparation of complexes. [b] Complex formation was determined by both IR and NMR spectroscopy. [c] Determined by integration of the NMR spectrum of the complex in Me_2SO-d_6 solution. Accuracy ±10%. [d] Complex prepared in 1:1 water–ethanol.

Cyclotricatechylene Inclusion Complexes. The preparation of the **1b**–dimethyl formamide (DMF) complex was typical for the complexes in Table I. Compound **1b** (0.25 g) was dissolved in 1.0 mL of freshly dried and distilled DMF. Diethyl ether was added dropwise to the resultant clear solution until clouding occurred. The mixture was then cooled and scratched. The resultant microcrystalline[8] complex was filtered off, washed with

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[†] Tables containing h, k, l, $|F_{obsd}|$, and $|F_{calcd}|$ values are available from this author upon request.

[1] H. M. Powell, "Non-Stoichiometric Compounds", L. Mandelcorn, Ed., Academic Press, 1964, Chapter 7.

[2] In a 1958 paper, Gaglioti et al.[3] described several clathrates of **1a**. Unfortunately, the structure ascribed to **1a** at that time is now known to be incorrect;[4a] therefore, the composition of their clathrates is unclear. We have been unable to prepare the benzene and acetone complexes of **1a** described by these authors.

[3] V. Gaglioti, A. Liquori, N. Gallo, E. Giglio, and M. Scrocco, *J. Inorg. Nucl. Chem.*, 8, 572 (1958).

[4] (a) A. S. Lindsey, *J. Chem. Soc.*, 1685 (1965); (b) A. Goldup, A. B. Morrison, and G. W. Smith, *ibid.*, 3864 (1965).

[5] The name "cyclotricatechylene" bears the same relationship to the parent "catechol" as does "cyclotriveratrylene" to "veratrol".

[6] J. A. Hyatt, *J. Org. Chem.*, 43, 1808 (1978).

[7] IR spectra were recorded on a Beckman Infracord instrument; NMR spectra were obtained with Varian EM-360 and JEOL MH-100 equipment.

[8] X-ray powder diffraction photographs showed that the complex is crystalline.

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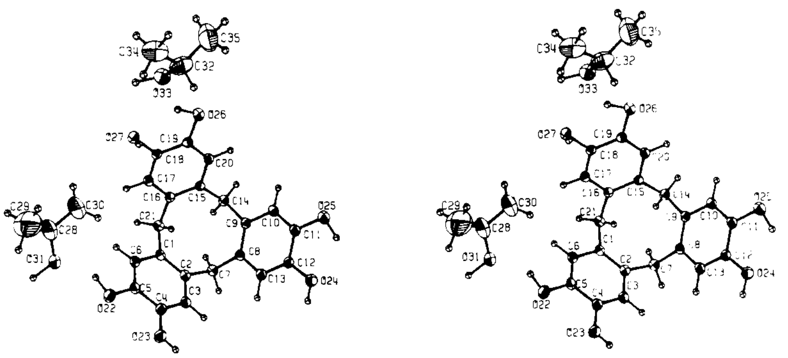

Figure 1. Stereoscopic view of **1b** and the two 2-propanol molecules. It should be noted that these 2-propanol molecules are not those whose coordinates are given in Table I.

Table II. Cyclotriveratrylene (1a) Inclusion Compounds[a]

guest molecule	complex[b]	ratio 1a: guest[c]
ethyl acetate	yes	1:1.6
methyl ethyl ketone	yes	1:3.2
methyl isobutyl ketone	no	
n-butyl acetate	no	
acetone	no	
N,*N*-dimethylformamide	no	
benzene	no	
ethanol	yes	1:1.5

[a] Complex prepared by recrystallization or evaporation from a solution in the guest compound. [b] Complex formation assayed by both IR and NMR spectroscopy. [c] Ratio determined by integration of the NMR spectrum of the complex in $CDCl_3$. Accuracy ±10%.

ether, and air-dried to constant weight to give 0.21 g of the complex 1:3 **1b**–DMF: IR (KBr) 2.9–3.8 (br), 6.01, 7.82 μm; NMR (Me_2SO-d_6) δ 7.90 (s, 3 H, DMF), 7.20 (br s, 6 H, OH), 6.61 (s, 6 H, Ar H of **1b**), 4.42 (d, *J* = 13 Hz, $-CH_2-$ of **1b**), 3.10 (d, *J* = 13 Hz, CH_2 of **1b**), 2.94 (s, 9 H, DMF), 2.81 (s, 9 H, DMF).

This complex was indefinitely stable upon storage in air or for up to ca. 6 h at 0.1 mmHg and 25 °C. If the complex was heated overnight at 70 °C in vacuum, DMF was lost and **1b** regenerated. Results are summarized in Table I.

Attempts to prepare crystals of cyclotricatechylene (**1b**) inclusion compounds from ethanol and DMF that would be suitable for single-crystal X-ray work were unsuccessful.

Cyclotriveratrylene complexes studied as above are described in Table II.

X-ray Analysis of Cyclotricatechylene Di-2-propanolate. Material obtained from evaporation of an ethanol solution of **1b** was dissolved in 2-propanol at ~80 °C. Thin (0.05–0.1 mm) crystals ranging in size up to 1.0 × 1.0 mm were obtained after slow evaporation for about 1 week. The crystals were clear, although they had a slight pinkish tinge, and they extinguished polarized light. Two crystals were used to accumulate the intensity data and they were coated with a thin layer of epoxy to reduce decomposition.

Crystal data: $C_{21}H_{18}O_6 \cdot 2C_3H_8O$; mol wt 486.6; triclinic; *a* = 9.605 (2), *b* = 9.819 (2), *c* = 13.737 (3) Å; α = 95.36 (2), β = 94.30 (2), γ = 99.54 (2)°; *V* = 1267 Å^3; *F*(000) = 520; *Z* = 2; D_c = 1.28 g cm^{-3}; space group $P\bar{1}$, μ(Mo Kα) = 1.0 cm^{-1}. Unit-cell parameters were obtained from a least-squares fit to the settings for 15 high-order reflections (λ(Mo Kα) = 0.7107 Å).

Intensity data were collected on a crystal (0.10 × 0.15 × 0.30 mm) with a variable 2θ scan out to 2θ = 60° (Mo Kα) on a Syntex $P2_1$ diffractometer. After 5 days of data collection, the crystal was noted to have turned black and the intensities of the standard reflections fell over a period of 8 h to zero. Data collection was continued on a second crystal (0.12 × 0.40 × 0.62 mm) without any evidence of decomposition during the period of data collection. A total of 5842 unique reflections in the hemisphere ±*h*, ±*k*, *l* was obtained from the two crystals; of these reflections, 3448 were considered to be significant at the 1.96σ(*I*) level. The data were scaled between the two crystals and corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by the use of the MULTAN program.[9] The positions of sufficient hydrogen atoms were obtained from difference maps to allow the remainder to be positioned according to standard criteria. Full-matrix least-squares refinement of the positional and anisotropic thermal parameters for the nonhydrogen atoms gave values of *R* and R_w of 0.075 and 0.077 on the nonzero reflections; the "goodness of fit" was 2.12.[10] The parameters for the hydrogen atoms were not refined. The reflections were weighted according to $1/[\sigma^2(F_o) + (0.02 \times F_o)^2]$.

The largest peak on a final difference map was 0.55 e/Å^3 and was within 0.3 Å from C(28), indicating some disorder in this 2-propanol group. No attempt was made to include disorder in the structural model. The scattering curves were those for the neutral atoms given by the analytical expression in the "International Tables for X-Ray Crystallography".[11] The final atomic coordinates are given in Table III.

Results and Discussion

When cyclotricatechylene (**1b**) was recrystallized or precipitated (by ether addition) from a number of amide, sulfone, and ketone solvents and from water, stable microcrystalline complexes, generally consisting of **1b** and the guest compound in a 1:3 ratio were obtained (see Table I). The complexes were indefinitely stable in air and lost the guest solvent only upon prolonged heating under vacuum. Infrared spectra of the solid complexes disclosed considerably broadened hydrogen-bonded hydroxyl absorptions, but the carbonyl absorptions due to the guest molecules were not appreciably shifted from their uncomplexed values. The guests ranged in size from water to *N*-methylpyrrolidinone and hexamethylphosphoric triamide. It is of interest that although 2-propanol formed a complex, ethanol did not.

The behavior of **1b** can be contrasted to that of its hexa-*O*-methyl ether, **1a**, which is far less prone to form inclusion compounds than is **1b**; in addition, the stoichiometry of the complexes of **1a** was generally far from 1:3 (see Table II).[3] That **1b** forms more, and better defined, complexes than does **1a** is consistent with the known tendency of phenolic compounds such as Dianin's molecule[12] and hydroquinone[13] to act as hosts. However, in our work catechol failed to form stable complexes with any of the variety of guests listed in Table I.

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(9) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, 27, 368 (1971).

(10) $R = \sum||F_{obsd}| - |F_{calcd}||/\sum|F_{obsd}|$; $R_w = [\sum w||F_{obsd}| - |F_{calcd}||^2/\sum w|F_{obsd}|^2]^{1/2}$; goodness of fit = $[\sum w|F_{obsd}| - |F_{calcd}|^2/(m - n)]^{1/2}$.

(11) "International Tables for X-Ray Crystallography", Vol. IV, W. C. Hamilton and J. A. Ibers, Eds., The Kynoch Press, Birmingham, England, 1974, pp 99–102.

(12) H. Powell and B. Wetters, *Chem. Ind. (London)*, **256** (1955); J. L. Flippen, J. Karle, and I. L. Karle, *J. Am. Chem. Soc.*, **92**, 3749 (1970).

(13) J. Boeyens and J. Pretorius, *Acta Crystallogr., Sect. B*, **33**, 2120 (1977).

Table III. Final Atomic Coordinates for the 1b-Di-2-propanolate Complex[a,b]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*	
C1	0.3918 (3)	0.4523 (3)	0.1250 (2)	H3	0.312 (0)	0.123 (8)	0.169 (0)	7 (0)
C2	0.3894 (3)	0.3355 (4)	0.1761 (2)	H6	0.323 (0)	0.519 (0)	−0.007 (0)	7 (0)
C3	0.3127 (3)	0.2072 (4)	0.1329 (3)	H7A	0.542 (0)	0.424 (0)	0.289 (0)	7 (0)
C4	0.2375 (3)	0.1940 (4)	0.0417 (3)	H7B	0.506 (0)	0.255 (0)	0.283 (0)	7 (0)
C5	0.2408 (3)	0.3101 (4)	−0.0095 (2)	H10	0.257 (0)	0.564 (0)	0.529 (0)	7 (0)
C6	0.3189 (3)	0.4367 (4)	0.0312 (3)	H13	0.298 (0)	0.138 (0)	0.347 (0)	7 (0)
C7	0.4643 (3)	0.3414 (4)	0.2786 (3)	H14A	0.521 (0)	0.608 (0)	0.363 (0)	7 (0)
C8	0.3676 (3)	0.3519 (4)	0.3602 (2)	H14B	0.449 (0)	0.684 (0)	0.453 (0)	7 (0)
C9	0.3538 (3)	0.4781 (3)	0.4127 (2)	H17	0.290 (0)	0.743 (0)	0.084 (0)	7 (0)
C10	0.2648 (3)	0.4748 (4)	0.4898 (3)	H20	0.231 (0)	0.770 (0)	0.424 (0)	7 (0)
C11	0.1888 (4)	0.3512 (4)	0.5115 (3)	H21A	0.543 (0)	0.591 (0)	0.216 (0)	7 (0)
C12	0.1972 (4)	0.2277 (4)	0.4571 (3)	H21B	0.501 (0)	0.649 (0)	0.112 (0)	7 (0)
C13	0.2883 (4)	0.2285 (4)	0.3838 (3)	OH22	0.176 (0)	0.382 (0)	−0.118 (0)	7 (0)
C14	0.4292 (3)	0.6203 (4)	0.3902 (3)	OH23	0.147 (0)	−0.000 (0)	0.024 (0)	7 (0)
C15	0.3439 (3)	0.6877 (3)	0.3166 (2)	OH24	0.088 (0)	0.029 (0)	0.441 (0)	7 (0)
C16	0.3611 (3)	0.6789 (3)	0.2166 (2)	OH25	0.062 (0)	0.245 (0)	0.590 (0)	7 (0)
C17	0.2761 (3)	0.7456 (3)	0.1559 (2)	OH26	−0.000 (0)	0.912 (0)	0.265 (0)	7 (0)
C18	0.1740 (3)	0.8146 (3)	0.1917 (2)	OH27	0.000 (0)	0.816 (0)	0.120 (0)	7 (0)
C19	0.1558 (3)	0.8238 (3)	0.2904 (3)	H28	−0.147 (0)	0.329 (0)	0.241 (0)	7 (0)
C20	0.2420 (3)	0.7616 (4)	0.3525 (2)	H29A	0.049 (0)	0.488 (0)	0.321 (0)	7 (0)
C21	0.4634 (3)	0.5981 (4)	0.1667 (3)	H29B	−0.029 (0)	0.311 (0)	0.307 (0)	7 (0)
O22	0.1638 (3)	0.2902 (3)	−0.0998 (2)	H29C	0.086 (0)	0.363 (0)	0.232 (0)	7 (0)
O23	0.1584 (3)	0.0715 (3)	−0.0029 (2)	H30A	−0.078 (0)	0.410 (0)	0.061 (0)	7 (0)
O24	0.1135 (3)	0.1114 (3)	0.4826 (2)	H30B	−0.032 (0)	0.276 (0)	0.102 (0)	7 (0)
O25	0.1044 (3)	0.3506 (3)	0.5889 (2)	H30C	−0.199 (0)	0.289 (0)	0.087 (0)	7 (0)
O26	0.0553 (2)	0.8912 (3)	0.3311 (2)	OH31	−0.147 (0)	0.559 (0)	0.294 (0)	7 (0)
O27	0.0931 (2)	0.8817 (2)	0.1294 (2)	H32	−0.311 (0)	−0.141 (0)	0.261 (0)	7 (0)
C28	−0.0931 (9)	0.4020 (8)	0.2051 (4)	OH33	−0.147 (0)	−0.000 (0)	0.147 (0)	7 (0)
C29	0.0066 (9)	0.3882 (9)	0.2676 (7)	H34A	−0.405 (0)	−0.086 (0)	0.123 (0)	7 (0)
C30	−0.1003 (11)	0.3420 (9)	0.1060 (5)	H34B	−0.355 (0)	0.083 (0)	0.154 (0)	7 (0)
O31	−0.1688 (3)	0.5125 (3)	0.2162 (2)	H34C	−0.484 (0)	−0.001 (0)	0.207 (0)	7 (0)
C32	−0.2877 (5)	−0.0389 (6)	0.2553 (5)	H35A	−0.412 (0)	0.029 (0)	0.382 (0)	7 (0)
O33	−0.1442 (3)	−0.0027 (3)	0.2261 (2)	H35B	−0.258 (0)	0.137 (0)	0.350 (0)	7 (0)
C34	−0.3917 (5)	−0.0068 (6)	0.1792 (5)	H35C	−0.235 (0)	−0.001 (0)	0.402 (0)	7 (0)
C35	−0.2964 (8)	0.0368 (9)	0.3535 (5)					

[a] Hydrogen atoms are given the number of the atoms to which they are attached. [b] If the standard deviation is zero, the parameter was not varied in the refinement.

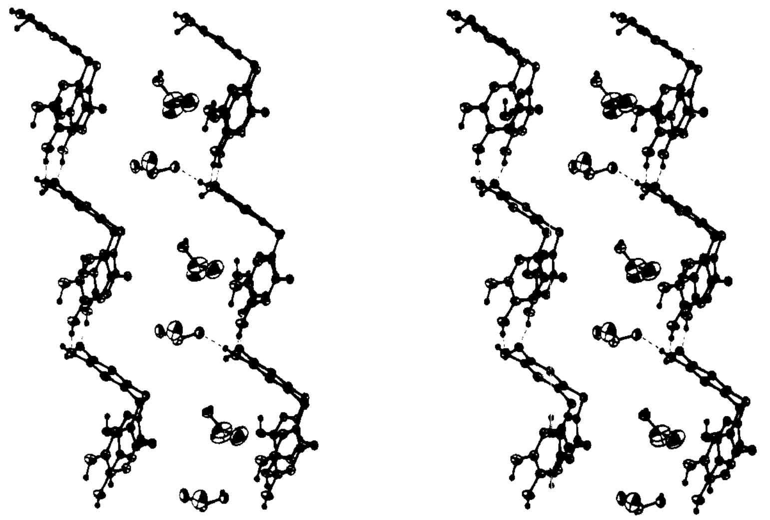

Figure 2. Stereoscopic view of the walls of the channel formed by adjacent rows of **1b** molecules. The channels are constricted such that there are pockets, each of which contains two 2-propanol molecules.

The ability of **1b** to form a variety of complexes together with the interest in the conformation of a compound with such an unusual nine-membered ring made an X-ray crystal structure of a complex of **1b** desirable. Crystals of a 1:2 cyclotricatechylene–2-propanol complex were found to be suitable and the X-ray structure was determined.

A stereoscopic view of a single molecule of cyclotricatechylene (**1b**) di-2-propanolate is shown in Figure 1. It should be noted that the two 2-propanol molecules shown in this figure are symmetry equivalent to those for which the coordinates are given in Table III.

Bond lengths and angles are given in Table IV. Apart from those in one of the 2-propanol molecules, the dimensions correspond to the expected values. The C(sp^3)–C(aromatic) distances range from 1.516 (5)–1.532 (5) Å, while the C–C distances in the phenyl rings are from 1.375 (4)–1.410 (5) Å.

Molecular Symmetry. It has been pointed out previously[4a] that, like cyclononatriene, **1a** (and by inference **1b**) can exist in a "crown" or a "saddle" conformation, the "crown" being favored both by energy considerations and,

Table IV. Bond Lengths (A) and Angles (deg) in the 1b-Di-2-propanolate Complex

C1-C2	1.397 (5)	C12-C13	1.382 (5)
C1-C6	1.402 (5)	C12-O24	1.373 (5)
C1-C21	1.521 (5)	C14-C15	1.521 (5)
C2-C3	1.403 (5)	C15-C16	1.392 (5)
C2-C7	1.524 (5)	C15-C20	1.403 (5)
C3-C4	1.382 (5)	C16-C17	1.402 (5)
C4-C5	1.391 (5)	C16-C21	1.524 (4)
C4-O23	1.374 (4)	C17-C18	1.375 (4)
C5-C6	1.385 (5)	C18-C19	1.376 (5)
C5-O22	1.375 (4)	C18-O27	1.394 (4)
C7-C8	1.516 (5)	C19-C20	1.395 (5)
C8-C9	1.406 (5)	C19-O26	1.380 (4)
C8-C13	1.399 (5)	C20-C29	1.271 (12)
C9-C10	1.410 (5)	C28-C30	1.424 (9)
C9-C14	1.532 (5)	C28-O31	1.406 (9)
C10-C11	1.379 (5)	C32-O33	1.462 (6)
C11-C12	1.381 (5)	C32-C34	1.483 (9)
C11-O25	1.385 (4)	C32-C35	1.494 (10)
C2-C1-C6	118.7 (3)	C13-C12-O24	125.0 (3)
C2-C1-C21	123.9 (3)	C13-C12-C11	119.2 (3)
C6-C1-C21	117.3 (3)	O24-C12-C11	115.8 (3)
C3-C2-C7	118.0 (3)	C8-C13-C12	121.8 (3)
C3-C2-C1	119.2 (3)	C15-C14-C9	113.8 (3)
C7-C2-C1	122.8 (3)	C16-C15-C20	119.3 (3)
C7-C3-C2	121.6 (3)	C16-C15-C14	123.6 (3)
C5-C4-O23	117.0 (3)	C20-C15-C14	117.4 (3)
C5-C4-C3	119.2 (3)	C17-C16-C21	116.9 (3)
O23-C4-C3	123.9 (3)	C17-C16-C15	118.3 (3)
C6-C5-O22	123.8 (3)	C21-C16-C15	124.8 (3)
C6-C5-C4	119.8 (3)	C18-C17-O16	122.1 (3)
O22-C5-C4	116.4 (3)	C19-C18-O27	119.4 (3)
C1-C6-C5	121.4 (3)	C19-C18-C17	120.1 (3)
C8-C7-C2	113.7 (3)	O27-C18-C17	120.5 (3)
C9-C8-C13	118.9 (3)	C20-C19-O26	118.2 (3)
C9-C8-C7	123.5 (3)	C20-C19-C18	118.7 (3)
C13-C8-C7	117.6 (3)	O26-C19-C18	123.1 (3)
C10-C9-C14	117.7 (3)	C15-C20-C19	121.7 (3)
C10-C9-C8	118.6 (3)	C1-C21-C16	112.0 (3)
C14-C9-C8	123.7 (3)	C29-C28-C30	120.9 (8)
C11-C10-C9	121.0 (3)	C29-C28-O31	122.1 (7)
C12-C11-O25	119.7 (3)	C30-C28-O31	113.0 (6)
C12-C11-C10	120.5 (3)	O33-C32-C34	109.8 (5)
O25-C11-C10	119.7 (3)	O33-C32-C35	109.1 (5)
		C34-C32-C35	112.3 (6)

in solution, by NMR studies of **1a** in deuteriochloroform. In Figure 1 a crown conformation is evident with the three phenyl rings all pointing toward the bottom of the crown, thus producing an approximate conical shape. Although inspection of molecular models suggests the possibility of threefold molecular symmetry, exact C_3 symmetry is not found in the crystal structure. The disposition of the hydroxyl groups is of special interest in this connection and appears to be the major factor destroying the threefold molecular symmetry axis.

The phenyl ring C(1)–C(6) has the O(22)–H and O(23)–H bonds in the plane of the ring but pointing away from each other; the C(8)–C(13) phenyl ring has the O(24)–H and O(25)–H bonds in the plane of the ring but oriented such that there is an O(25)–H- - -O(24) intramolecular hydrogen bond although there is also an intermolecular hydrogen bond; in the C(15)–C(20) phenyl ring the O(26)–H bond is in the plane of the phenyl ring and appears to be involved in a bifurcated hydrogen bond, intramolecularly to O(27) and to an O(33) of a 2-propanol molecule, while the O(27)–H bond is atypically twisted out of the plane of the ring by 77°. If the O(27)–H bond were in the plane of the ring there would be an unacceptably short contact between H(27) and the hydrogen atoms of a methyl group of a 2-propanol molecule. In addition, the orientation of the O(27)–H bond plays an important role in the construction of the channel.

Structure and Shape of the Cavity. A stereoscopic view of the length of the channel is shown in Figure 2. The two "walls" of the channel shown in this figure consist of two adjacent rows of molecules of **1b** translationally related in the *a* direction. The 2-propanol molecules are "sandwiched" between these two rows. The channel axis runs along the *b* direction and each wall of the channel is maintained by two hydrogen bonds, O(23)–H- - -O(27) (*x*, −1 + *y*, *z*) and O(24)–H- - -O(26) (*x*, −1 + *y*, *z*) (see Table V), between molecules translationally related in the *b* direction. The sides of the channel are completed by centrosymmetrically related molecules of **1b**. A cross section of the channel is shown in Figure 3. The molecules of the wall which have their concave side facing the channel form two pairs of centrosymmetrically related hydrogen bonds to the two molecules that form the sides of the channel. The hydroxyl group O(27)–H forms a hydrogen bond to O(22) in the molecule at −*x*, 1 − *y*, *z*, thus completing one side and the hydroxyl group O(25)–H forms part of a bifurcated hydrogen bond O(26) in the molecule at −*x*, 1 − *y*, 1 − *z* to form the other side. For dimensions of the hydrogen bonds, see Table V. There are no hydrogen bonds between the "wall" of the channel with the molecules whose convex side faces the channel and the molecules that form the sides.

One of the 2-propanol molecules (C_{28}–O_{31}) forms a hydrogen bond to O(25) in a molecule in a side of the channel and accepts a hydrogen bond for O(22)–H from a molecule on the other side. The other 2-propanol molecule (C_{32}–O_{33}) forms a hydrogen bond to O(23) in a molecule in a side of the channel while it accepts one from O(26) from one of the walls. There is no hydrogen bonding between 2-propanol molecules in the channel. Inspection of Figure 3 shows that the channel is greatly constricted by the two hydroxyl groups (O(25)–H and O(22)–H) from the molecules of **1b** on respective sides of the channel and that there would be no opportunity for 2-propanol molecules to pass through the channel. Indeed the "channel" is really a

Table V. Hydrogen-Bonding Assignments and Dimensions

	transformation	O---O, Å	H---O,[a] Å	O-H---O,[a] deg
O(22)-H---O(31)	−*x*, 1 − *y*, −*z*	2.622 (4)	1.78	146
O(23)-H---O(27)	*x*, −1 + *y*, *z*	2.755 (3)	1.98	156
O(24)-H---O(26)	*x*, −1 + *y*, *z*	2.812 (4)	1.91	165
O(25)-H---O(24)[b]	intramolecular	2.665 (4)	2.03	116
O(25)-H---O(26)[b]	−*x*, 1 − *y*, 1 − *z*	2.955 (4)	2.04	143
O(26)-H---O(33)[b]	*x*, 1 + *y*, *z*	2.714 (4)	1.80	140
O(26)-H---O(27)[b]	intramolecular	2.816 (4)	2.14	119
O(27)-H---O(22)	−*x*, 1 − *y*, −*z*	2.728 (3)	1.73	177
O(31)-H---O(25)	−*x*, 1 − *y*, 1 − *z*	2.856 (4)	1.75	173
O(33)-H---O(23)	−*x*, −*y*, −*z*	3.066 (4)	2.03	159

[a] As the hydroxyl hydrogen atoms were not varied in the refinement but positioned from a difference map, there are no standard deviations for the dimensions involving hydrogen. While the hydrogen positions have not been corrected, the range of O-H values (0.82-1.107 Å) is not unreasonable. [b] These correspond to bifurcated hydrogen bonds.

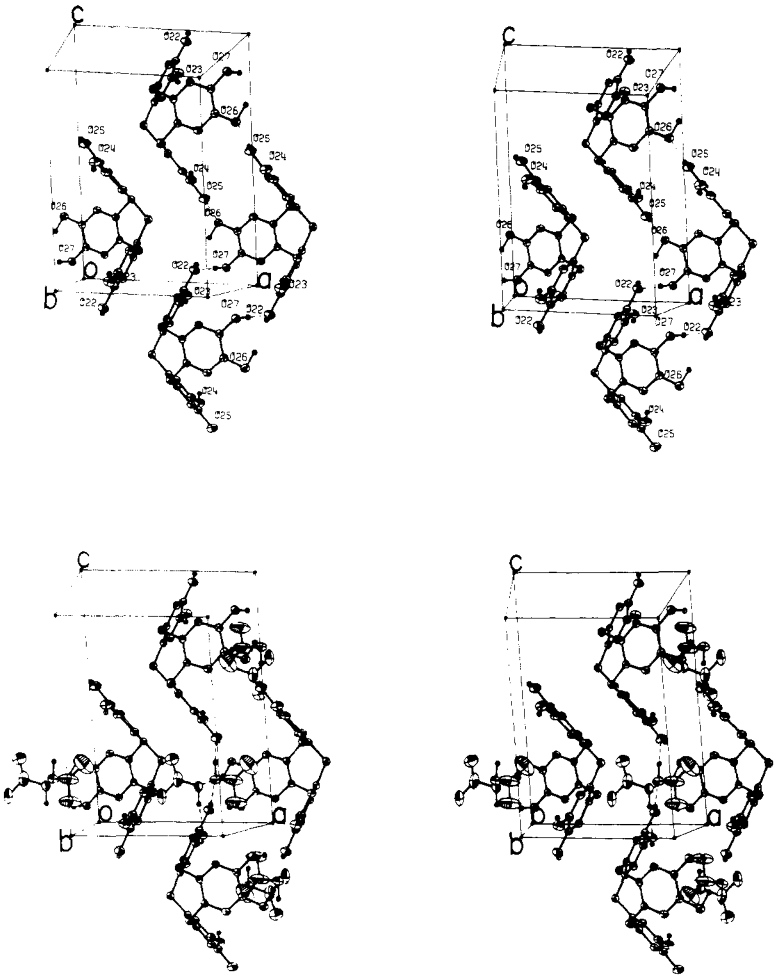

Figure 3. Stereoscopic views of the cross section of the channel (top) showing the hydrogen bonding (discontinuous lines) between the molecules of **1b** but omitting the 2-propanol molecules (the oxygen atoms of the **1b** molecules are numbered) and (bottom) showing the 2-propanol molecules in the channel. Hydrogen bonds between the 2-propanol molecules and the **1b** molecules are shown by discontinuous lines. The 2-propanol molecule nearer the viewer is the one that shows disorder.

series of cavities, each holding two 2-propanol molecules; for another such example, see ref 14.

It is apparent from the dimensions of the 2-propanol molecule C(28)–O(31) that it exhibits disorder in the crystal. The bond lengths are anomalous (e.g., C(28)–C(29), 1.271 (12) Å) and C(28) lies only 0.156 Å from the plane defined by C(29), C(30), and O(31) as compared to 0.470 Å for the corresponding distance for C(32). As O(31) is involved as a donor and acceptor in hydrogen bonding, the disorder probably arises from the 2-propyl group taking, at least, two positions while leaving the –O–H group invariant. If one examines the nonbonded contacts it appears that the 2-propyl group sits in the concave cavity of one of the cyclotricatechylene molecules. From Figure 3 and from the schematic drawing of the channel shown in Figure 4, it is seen that the disordered 2-propanol sits in the cavity and is surrounded by **1b** molecules, whereas the ordered one is located at the junction of the hydroxyl groups of four **1b** molecules that create the cross section of the channel.

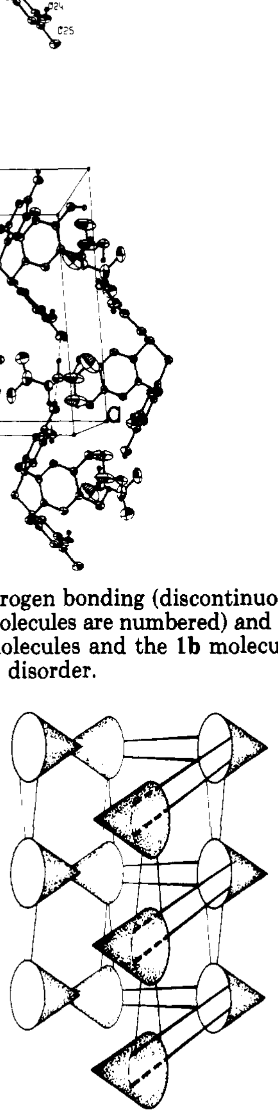

Figure 4. Schematic drawing of molecules of **1b** that provide the channel. **1b** molecules are shown as cones. Hydrogen bonds between **1b** molecules are shown as solid lines.

The structures of **1a** and **1b** are sufficiently close to that of one of the most prolific complexing compounds, *o*-trithymotide (**2**), to warrant discussion.[1,10,16] Trithymotide (**2**), with a 12-membered ring joining the three component benzene rings has considerably more flexibility than **1a** and this has been considered the basis of the ability of **2** to complex with guests varying in molecular size from methanol to such bulky molecules as *trans*-stilbene or *N*-alanyldinitroaniline. It has been pointed out that **2** has over 80 characterized complexes.[15b]

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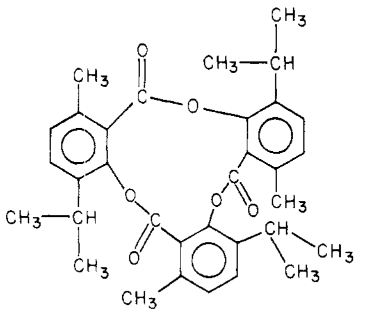

2

The rigidity of **1a** would seem to be responsible, at least in part, for its much more limited complexing ability, although this is countered by the hydrogen-bonding capability of **1b**. In any case, **1b** provides a potentially valuable addition to the collection of complexing agents, each of which has its own specific selectivity in the choice of guest molecules.

Acknowledgment. We thank the National Science Foundation for partial support of this work.

Registry No. **1a**·ethyl acetate, 75234-34-3; **1a**·methyl ethyl ketone, 75234-35-4; **1a**·ethanol, 75234-36-5; **1b**·*N*,*N*-dimethylformamide, 75247-87-9; **1b**·*N*-methylpyrrolidinone, 75247-88-0; **1b**·*N*,*N*-dimethylacetamide, 75247-89-1; **1b**·dimethyl sulfoxide, 75247-90-4; **1b**·water, 75247-91-5; **1b**·hexamethylphosphoric triamide, 75247-92-6; **1b**·acetone, 75247-93-7; **1b**·2-propanol, 75247-94-8.

Supplementary Material Available: Thermal parameters and intermolecular contacts for the **1b**–2-propanol complex (6 pages). Ordering information is given on any current masthead page.

Unique Bisannelation Strategy. Total Synthesis of Epizonarene, Clarification of Cadalane Stereochemistry, and Allylic Strain

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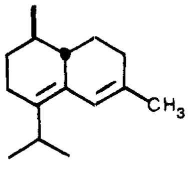
Bicyclic γ,δ-unsaturated ketones **3**, **5**, **15a**, and **15b** obtained via intramolecular Diels–Alder cyclizations were found to undergo acid-catalyzed isomerization to the corresponding α,β-unsaturated ketones in high yield. Ketone **15b** was isomerized to a 78:22 equilibrium mixture of enones **16b** and **16a**, respectively. The isopropyl stereochemistry was unequivocally established as pseudoequatorial in the minor isomer, **16a**, by X-ray diffraction. The mixture of **16a,b** has been converted to the natural product epizonarene (**1**).

The sesquiterpene epizonarene (**1**)[2] is a member of the cadalane class and has recently been synthesized[3] via ketone **2**. In this report, we use the synthesis of **2** to illustrate a new approach to enone synthesis based on the intramolecular Diels–Alder reaction.[4] The overall sequence in eq 1 presents this unique strategy for cyclohexenone annelation which is based on the fact that bicyclic γ,δ-unsaturated ketones can be isomerized into α,β-unsaturated ketones.



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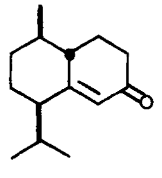

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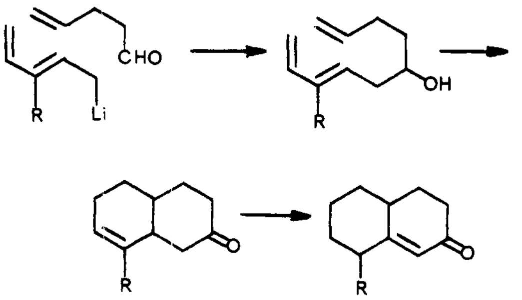

(1)

General Method

We recently reported the preparation of **3** which was used in a synthesis of (±)-selenadiene.[4b] When **3** was treated[5] with 5% H_2SO_4 in acetic acid[6,7] the double bond cleanly isomerized into conjugation with the ketone, yielding compound **4** (96%).[8] Compound **4** was exclusively the isomer with the quasi-equatorial methyl group and, surprisingly, can not readily be made by Robinson annelation.[9]

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(1) Address correspondence to this author at the Department of Chemistry, New York University, Washington Square, New York, NY 10003.

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(5) See the paragraph at the end of this paper regarding supplemental data.

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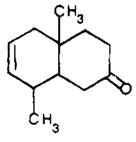

i

(8) Compound **4** is a natural product. Maurer, B.; Fracheboud, M.; Grieder, A.; Ohloff, G. *Helv. Chim. Acta* **1972**, *55*, 2371–2382.

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