Complexation with Hydroxy Host Compounds. 3.[1] Structures and Thermal Analysis of the Inclusion Compounds of Tri(1-naphthyl)silanol with Toluene, *o*-Xylene, *m*-Xylene, and *p*-Xylene

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Crystal structures of tri(1-naphthyl)silanol with toluene (1:1) (1), *o*-xylene (1:1) (2), *m*-xylene (1:1) (3) and *p*-xylene (1:2) (4) have been determined and compared. Crystal data are as follows. 1: $P\bar{1}$, $a = 9.465$ (3) Å, $b = 12.424$ (2) Å, $c = 13.344$ (4) Å, $\alpha = 116.08$ (2)°, $\beta = 91.67$ (2)°, $\gamma = 92.27$ (2)°; $Z = 2$. 2: $P\bar{1}$, $a = 9.399$ (5) Å, $b = 12.475$ (6) Å, $c = 13.577$ (5) Å, $\alpha = 115.96$ (4)°, $\beta = 90.37$ (4)°, $\gamma = 92.77$ (2)°; $Z = 2$. 3: $P\bar{1}$, $a = 11.974$ (3) Å, $b = 12.243$ (2) Å, $c = 12.317$ (2) Å, $\alpha = 65.16$ (1)°, $\beta = 72.50$ (2)°, $\gamma = 61.85$ (2)°, $Z = 2$. 4: $P\bar{1}$, $a = 9.315$ (6) Å, $b = 12.462$ (1) Å, $c = 15.901$ (4) Å, $\alpha = 82.51$ (2)°, $\beta = 82.08$ (4)°, $\gamma = 87.25$ (5)°, $Z = 2$. Possible hydrogen bonding between the hydroxyl group of the host and the aromatic π electrons of the guests was observed and confirmed by shifts in the infrared spectra of the compounds. Thermal analysis revealed the strength of binding of the guest species. The intermolecular nonbonded potential energies were calculated and a correlation observed between these and the enthalpy change of guest release for 2 and 3. Thermogravimetry was used to evaluate the activation energy of the guest release reaction in 1–4.

Clathrates and inclusion compounds have been extensively studied for their properties of storing or separating guest compounds.[2,3] Using these properties, a host compound may be used to separate isomers,[4] tautomers,[5] or enantiomers.[6,7] Compounds with bulky substituents and one or more hydroxyl groups have proved to be versatile hosts with a number of guest molecules.[2] These inclusion compounds usually involve a network of hydrogen bonds.

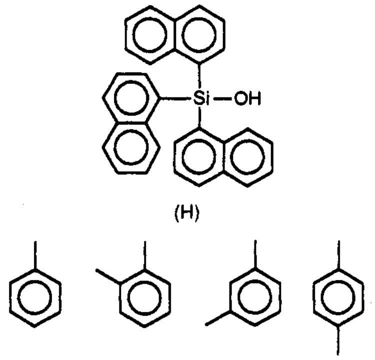
We have studied the hydroxy host tri(1-naphthyl)silanol and its inclusion behavior with guests which have hydrogen-bonding abilities such as dimethyl sulfoxide, dioxane, and triethylamine. We have reported[1] the structure of the molecular inclusion complex of the related host triphenylsilanol with ethanol.

We now present the results of a study of the enclathration behavior of trinaphthylsilanol with three isomers, *o*-xylene, *m*-xylene, and *p*-xylene, and with toluene.

The thermal analysis of the molecular complexes are discussed as well as the results of some preliminary energy studies.

Results and Discussion

Crystallography. Atomic coordinates of 1–4 are available as supplementary material. Bond lengths and angles fell within the range of literature values and are also available as supplementary material. The host conformation is similar in all four structures. The naphthyl rings of the host are always planar; the maximum deviation from their mean planes is 0.03 Å. In each structure, the naphthyl rings are not quite perpendicular to each other, with dihedral angles ranging from 70° to 83°. The Si atom of each host lies at the center of an irregular tetrahedron with bond angles around the Si falling within the range 107.1–112.6°. The guest molecules in 1–4 are also essentially planar—the maximum deviation from the mean plane is 0.03 Å, found in compound 2.



(H)

1, H•toluene
2, H•*o*-xylene
3, H•*m*-xylene
4, H•2(*p*-xylene)

Compounds 1 and 2 are similar. Guest molecules (either toluene or *o*-xylene) lie in hourglass-shaped channels parallel to [100] which have constrictions of approximately 1.5 Å at $x = 0$. Figure 1a shows the packing of these compounds, viewed down [100]. In this view the guest is seen edge-on.

Compound 3 is structurally similar to 1 and 2 in that each host is associated with one *m*-xylene molecule. Guests lie in cavities which are connected by narrow channels (Figure 1b).

Compound 4 differs from the other three in that the host to guest ratio is 1:2. Within the crystal structure, guest molecules occupy three crystallographically different sites. The guest *p*-xylene molecules lie in criss-crossing channels which run parallel to [001] and parallel to [010]. These can be seen in Figure 1c.

There is evidence for hydrogen bonding between the hydroxyl group of the trinaphthylsilanol and the aromatic

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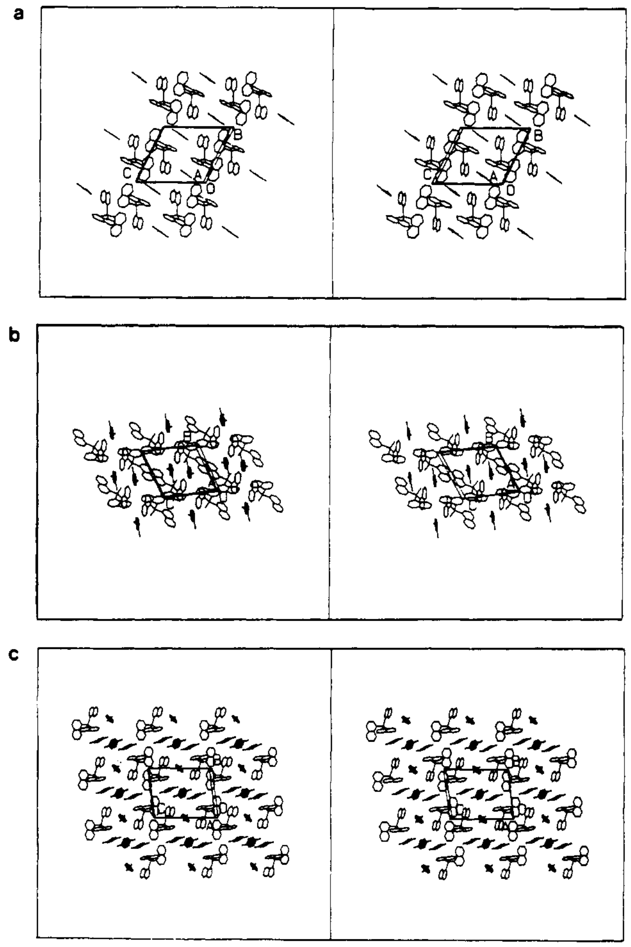

Figure 1. Packing diagrams of (a) 1, (b) 3, and (c) 4, all viewed down [100]. Guest molecules are shaded.

π electrons of the guest molecules. A similar form of hydrogen bonding has recently been reported.[8] An X-ray diffraction study of the Na_4[calix[4]arene sulfonate]·$13.5H_2O$ structure found a water molecule embedded in the cavity of four aromatic groups. The oxygen atom was 3.16 and 3.19 Å from the centroids of the nearest aromatic rings. Centroid···H-O angles were 133° and 127°.

The centroid···O distances for compounds 1 (and 2), 3, and 4 are 3.40, 3.66, and 3.28 Å, respectively. (Only one of the three crystallographically independent guests in 4 (guest A) is correctly positioned to participate in the π hydrogen bonding scheme.) The centroid···H separations are 2.58, 2.93, and 2.48 Å, with centroid···H-O angles of 160°, 143°, and 148°, respectively.

Further evidence that these compounds contain hydrogen bonds was found on examining the infrared spectra of these and related compounds. The O-H stretching band in the unsolvated host compound appears at 3670 cm^{-1}. For compounds 1-4 this band was shifted to 3605, 3610, 3620, and 3590 cm^{-1}, respectively. This shift is to be expected if the O-H group participates in a hydrogen bond. The shift is not as large as that found in similar compounds where the guest contains an acceptor atom. For example, the tri(1-naphthyl)silanol complexes with DMSO and dioxane have bands at 3520 and 3540 cm^{-1}, respectively. We note that there is a correlation between the O-H stretching frequency and the centroid···H-O distance, which gives further credence to the presence of hydrogen bonding.

Thermal Analysis. The objective of carrying out thermal analysis of these compounds is to reconcile thermodynamics with structure. Thus, it should, in principle, be possible to find a relation between the measured enthalpies of the guest release reactions and the host-guest interactions which occur in the crystal structure. The potential energy environment of the guest molecules in the lattice made up of host molecules was evaluated using the method of atom-atom potentials. We used the program EENY[9] to evaluate the van der Waals energy using empirical atom pair potential curves. The coefficients of the atom-atom potential are of the form

$$U(r) = a\ \exp((-br)/r^d - c/r^6)$$

where r is the distance between any pair of atoms and the coefficients a, b, c, and d are those given by Giglio.[10] These potential curves were derived primarily to give good agreement for calculation of molecular position in crystal structure. Minimization of energy was performed by the method of "steepest descent". No account was taken of partial atomic charges or dipole interactions, and the energy values derived are not absolute but can be used for comparing similar structures.

The host and guest molecules were placed in their crystallographically determined positions. Symmetry-related host molecules were generated so that the guest was completely surrounded. The positions of the hosts were held constant while the guest was allowed to find its minimum energy environment by incremental translations and rotations. The minimum potential energies thus obtained, U_{min}, are given in Table II. In compound 4 there are three crystallographically independent guest molecules. The minimization for a given guest was carried out by surrounding it by an appropriate number of host and other guest molecules. For all compounds, the final position of the guest was found to be very close to that of the crystallographically determined position.

The results of the thermal analysis are shown in the supplementary material. The first endotherm in the DSC curves (Figure 1sa-d) indicate that the desorption of guest occurs in a single step, while the second endotherm corresponds to the melting point of the host compound.

Another parameter of thermal stability is the temperature characterizing the start of the endothermic guest-release reaction, T_{on}. For inclusion compounds comprising a host with different guests, the onset temperatures are a function of both the host-guest nonbonding interactions and the intrinsic physical properties of the guest itself. In particular, the normal boiling point T_b of the guest compound is important and we may use $T_{on}-T_b$ as a measure of the relative stabilities of the inclusion compounds. These are listed in Table II.

The thermal gravimetry experiments were carried out at various heating rates in order to study the activation energy of the reaction.[11] In this method the temperatures of decomposition at a fixed percentage weight loss are measured at the various heating rates. A plot of the logarithm of the heating rate (β) versus the reciprocal of the absolute temperature is examined. If parallel straight lines are obtained a single step decomposition reaction is indicated, and the slope of the lines is directly related to the activation energy of the desorption reaction. This method, originally developed for the thermal decomposition of polymers, has also been applied to the decomposition of

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Table I. Crystal Data and Experimental and Refinement Parameters for the Structure Analysis

	1	2	3	4
molecular formula	$C_{30}H_{22}OSi{\cdot}C_7H_8$	$C_{30}H_{22}OSi{\cdot}C_8H_{10}$	$C_{30}H_{22}OSi{\cdot}C_8H_{10}$	$C_{30}H_{22}OSi{\cdot}2(C_8H_{10})$
formula weight, g mol^{-1}	518.7	532.8	532.8	638.9
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	9.465 (3)	9.399 (5)	11.974 (3)	9.315 (6)
b, Å	12.424 (2)	12.475 (6)	12.243 (2)	12.462 (1)
c, Å	13.344 (4)	13.577 (5)	12.317 (2)	15.901 (4)
α, deg	116.08 (2)	115.96 (4)	65.16 (1)	82.51 (2)
β, deg	91.67 (2)	90.37 (4)	72.50 (2)	82.08 (4)
γ, deg	92.77 (2)	92.71 (4)	61.85 (2)	87.25 (5)
V, Å^3	1405.56	1429.05	1432.74	1811.91
Z	2	2	2	2
D_c, g cm^{-3}	1.23	1.24	1.24	1.17
D_m, g cm^{-3}	1.21	1.23	1.22	1.15
range scanned, max θ	23	25	25	25
no. of reflns collected	4113	5252	5305	6455
reflns with $I_{rel} > 2\sigma I_{rel}$	2958	2735	4086	3856
absorption coefficient, Mo K_α, cm^{-1}	1.06	0.75	1.06	0.94
data to parameter ratio	8.0	7.0	10.4	8.1
R	0.0591	0.0804	0.0381	0.0480
R_w	0.0690	0.0769	0.0443	0.0572
g ($w = (\sigma^2F + gF^2)^{-1}$)	0.002	0.005	0.001	0.005
max height in emap (e Å^{-3})	0.83	0.30	0.20	0.30
min height in emap (e Å^{-3})	−0.22	−0.44	−0.25	−0.20

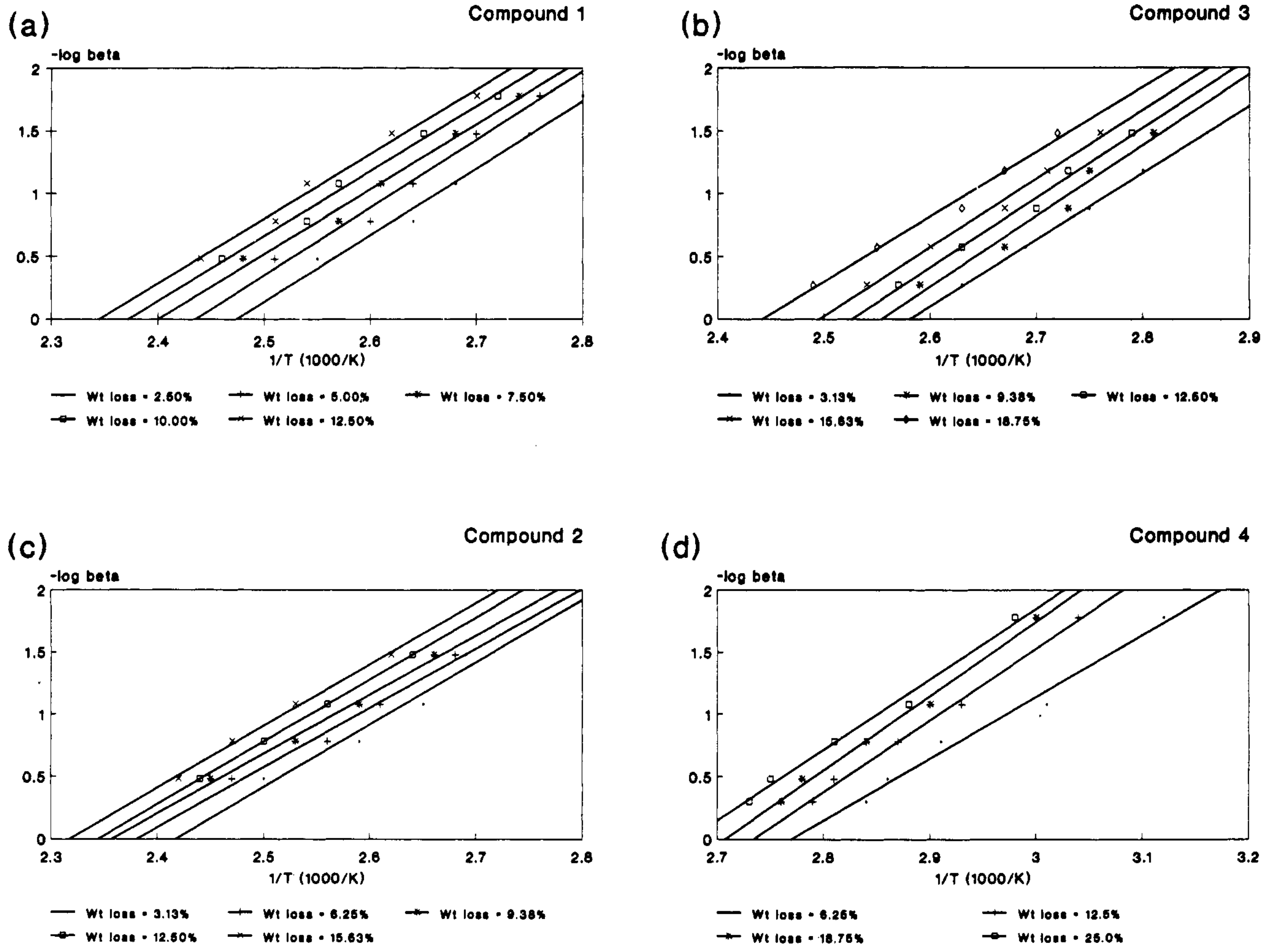

Figure 2. Plots of −log β against $1/T$ which were used to calculate E_A for guest desorption in **1**–**4**.

inorganic coordination compounds.[12] The TG curves are shown in the supplementary material. The observed total weight losses are in excellent agreement with the calculated values, thus confirming the adopted host to guest ratios. The corresponding semilogarithmic plots are shown in Figure 2 and the activation energies thus derived are listed in Table II.

When an inclusion compound is heated and the guest molecules are allowed to escape, the host may revert to the nonporous α-phase, or the host framework may hold, giving rise to an empty clathrate, or β_0-phase.[13] A well-known

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Table II. Thermal Analysis

compd	1	2	3	4
guest	toluene	*o*-xylene	*m*-xylene	*p*-xylene
host:guest	1:1	1:1	1:1	1:2
TG wt loss (calcd), %	17.8	19.9	19.9	33.2
TG wt loss (obs), %	17.6	19.5	17.5	32.8
$T_{on} - T_b$, K	−22.6	−42.9	−62.1	−66.9
ΔH (kJ mol^{-1})[a]	33.2	61.6	49.3	42.3
U_{min} (kJ mol^{-1})	−68.4	−74.7	−63.1	−73.0, −47.0, −67.0
E_A (kJ mol^{-1})	94 ± 2	89 ± 2	100 ± 4	102 ± 7

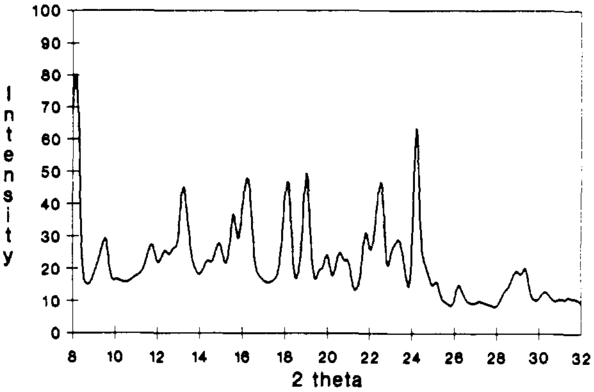
[a] Errors in the ΔH values can be as high as 20% owing to the difficulties in reproducing the sample preparations.

example of the latter phenomenon occurs with zeolites, which can be dehydrated by heating to elevated temperatures under vacuum without significant damage to the silica/alumina framework.[14] With the vast majority of inclusion compounds where the hosts are discrete organic molecules, however, this latter process is rare, and the structure of the host–guest compound, β-phase, usually collapses to the α-phase on guest loss. The X-ray powder diffraction patterns of compound 1 are shown in Figure 3 [(a) freshly removed from the mother liquor and crushed (β-phase); (b) crushed and maintained at 110 °C in vacuo for 1 h to ensure complete guest loss; (c) the pattern obtained from the pure host crystallized from chloroform]. The pattern shown in Figure 3b is more like that of the α-phase (Figure 3c) than that of the β-phase (Figure 3a). The desorption of the guest from compound 1, then, seems to leave a framework of host molecules similar to that found in the unsolvated host compound.

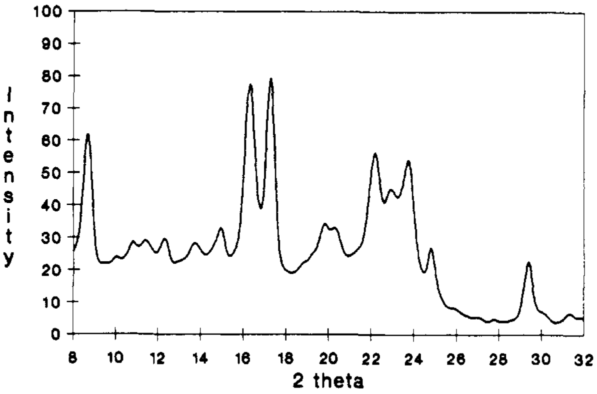
Table II summarizes the structural and thermodynamic results. One might expect that the compounds showing the greater stability would have the lowest crystal energy, U_{min}, and the highest values of T_{on} − T_b and of ΔH, the enthalpy change of the guest release reaction. The results of the energy calculation must, however, be interpreted with caution because comparison of host–guest interactions should strictly only be carried out between guests which are geometrical isomers and between compounds which have the same host to guest ratio. Comparison can therefore be made between compounds 2 and 3, and Table II shows 2 to be the more stable, with the lowest U_{min} and the highest values of T_{on} − T_b and ΔH.

The activation energies of the decomposition reactions of the four compounds vary between 89 and 102 kJ mol^{-1} and are similar to those found in the decomposition of the inclusion compounds formed by *trans*-9,10-dihydroxy-9,10-dihydroanthracene with acetonitrile, 2,4-dimethylpyridine, and 2,6-dimethylpyridine, which yield activation energies from 70 to 115 kJ mol^{-1}.[15] We have calculated the packing factors of structures 1 and 2 as the volume in Å^{-3} per non-hydrogen atom. We note that 1, with a packing factor of 18.02 Å^{-3}/atom is not as well packed as 2, which has a packing factor of 17.86 Å^{-3}/atom. However, the activation energy of desorption is greater for 1 than for 2 and we regard this as unusual.

(a) Compound 1



(b) Compound 1 (dried)



(c) Trinaphthylsilanol

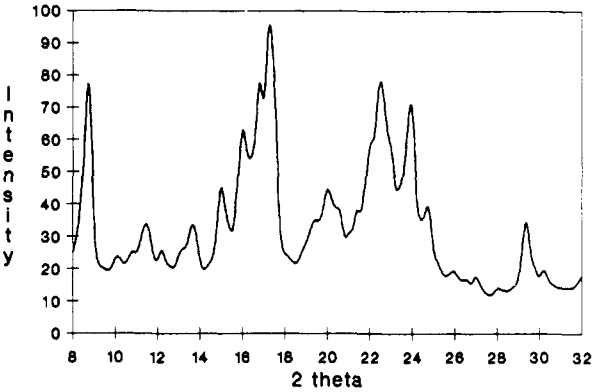


Figure 3. X-ray powder diffraction patterns: (a) 1 freshly removed from mother liquor and crushed (β-phase); (b) 1 crushed and maintained at 110 °C for 1 h to ensure complete guest loss; and (c) trinaphthylsilanol (α-phase).

Experimental Section

Synthesis. Tri(1-naphthyl)silanol (H, host compound) was synthesized in one step, unlike the literature procedure.[16] To a stirred solution of 44.0 g (0.21 mol) 1-bromonaphthalene in 100 mL of dry Et_2O was added 131.2 mL (0.21 mol) of *n*-BuLi (1.6 N in *n*-hexane) at such a rate as to keep the temperature between 0 and 5 °C under an atmosphere of argon. After the solution was stirred for 20 min, a solution of 10.2 g (60 mmol) of $SiCl_4$ in 50 mL of dry Et_2O was added under the same temperature conditions. Stirring was continued for 2 h at this temperature before the mixture was poured onto 100 mL of diluted HCl. The precipitate which formed was collected and washed with a few mL of cold MeOH. The organic layer was separated, washed with

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H_2O, and dried (Na_2SO_4). Evaporation of the solvent yielded a viscous oil which solidified on addition of a few mL of EtOH. The two crops of solids were combined and recrystallized from toluene to give the 1:1 clathrate which was decomposed under vacuum (15 Torr) and heating (100 °C) to yield the pure host compound; 53%, mp 209–211 °C (lit.[16] mp 208–209 °C).

Crystal Structure Determination. Data Collection and Processing. The inclusion compounds **1–4** were obtained by dissolving the host (H) in a minimum amount of chloroform and adding an excess of the appropriate guest liquid.

The solutions were allowed to evaporate slowly for 3–4 days until crystals formed. These were mounted in capillary tubes and sealed under an atmosphere of mother liquor. Details of the crystallographic data collection and refinement for compounds **1–4** are summarized in Table I. Preliminary cell dimensions were determined photographically. Data were collected at 293 K on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo K_α ($\lambda = 0.7107$ Å) radiation and the $\omega - 2\theta$ method. Crystal stabilities were checked by periodic monitoring of three reference reflections. Data were corrected by Lorentz and polarization factors, and absorption corrections were applied.[17] Final refinements were based on those observations that satisfied the condition $I > 2\sigma I$.

Solution and Refinement. The structures were solved by direct methods using SHELXS-86.[18] They were then refined by full-matrix least-squares using the SHELX76 program system.[19] Non-hydrogen atoms were treated anisotropically, and non-hydroxyl hydrogens were constrained to 1.00 Å from their parent atoms. Approximate positions for the hydroxyl hydrogens were found in difference Fourier maps, and these were then included in the structures at fixed distances from their parent oxygens. The final difference Fourier maps showed no indication of incorrectly placed or missing atoms.

Thermal Analysis. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed using a Perkin-Elmer PC7 series system. Before analysis, crystals were removed from their mother liquor, blotted dry on filter paper, and crushed. Sample weight, in each case, was approximately 5 mg. A constant stream of nitrogen (flow rate 40 mL min^{-1}) was passed over the samples. The temperature range for the DSC was typically 30–250 °C at a heating rate of 10 °C min^{-1}.

TG was used to confirm the host to guest stoichiometry determined by crystal structure analysis. It was also used to calculate an approximate value for the activation energy of guest desorption, using the method described by Flynn and Wall.[11] Various heating rates in the range 1–35 °C min^{-1} were used.

Acknowledgment. L.N. and S.B. thank the University of Cape Town and the Foundation for Research Development (Pretoria) for research grants. E.W. thanks the Deutsche Forschungsgemeinschaft (SFB 334) and the Fonds der Chemischen Industrie for financial support. K.S. thanks the Konrad Adenauer Foundation for a scholarship.

Registry No. 1, 139276-41-8; 2, 139276-42-9; 3, 139276-43-0; 4, 139276-44-1; tri(1-naphthyl)silanol, 18919-22-7; 1-bromonaphthalene, 90-11-9.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates, figures of DSC traces of **1–4** (onset temperatures of endotherms are marked), and TG curves of **1–4** (showing the change in onset temperatures with heating rate) (42 pages). Ordering information is given on any current masthead page. Observed and calculated structure factors are available directly from L.N.

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Proximity Effects in Fused Cyclobutanones. Facile Formation of Cage Systems[†,1]

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Chlorobicyclooctanone **3** on reaction with H_2O–Et_3N in acetonitrile at 20 °C produced in high yield four complex dimeric compounds **4–7**. The novel structures produced by C–C bond formation between tertiary centers were revealed by NMR and X-ray diffraction. Pathways leading from **4** or its diastereomer **14** to cage compounds **5–7** indicate the importance of proximity effects in these transformations.

α-Halocyclobutanones[2] have found wide synthetic application in the synthesis of tropolones,[3] α-methylene γ-lactones,[4] substituted cyclopentanones,[5] and even cyclopropane derivatives.[6] Reaction of bicyclic α-halocyclobutanones with nucleophiles can lead to ring opening,[7] ring contraction,[6] or cine substitution.[6c,8]

Recently,[9] we have shown that α-chlorobicyclooctanone **1** on reaction with hydroxide ion at room temperature (24 h) produced a cine substitution product **2** as well as a dimeric compound **2a**. The facile formation of a C–C bond between two tertiary centers can be attributed to coupling of an enolate with an oxidoallyl cation generated from **1**.

When we tried to test the generality of this coupling process by applying it to the oxabicyclooctane analogue

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[†] Dedicated to Prof. H. C. Brown on the occasion of his 80th birthday.

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