Acyclic Congener of Cucurbituril: Synthesis and Recognition Properties – Supporting Information
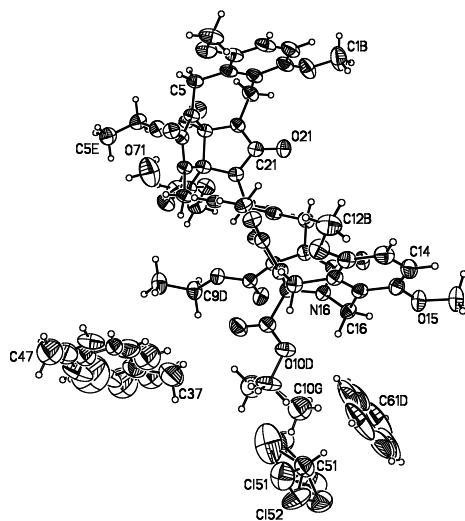
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General Experimental Procedures. Starting materials were purchased from commercial suppliers and were used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (230 - 400 mesh, 0.040-0.063 μm) using eluents in the indicated v:v ratio. Melting points were measured in open capillary tubes and are uncorrected. IR spectra were recorded as KBr pellets and are reported in cm^{-1}. NMR spectra were measured on spectrophotometers operating at 400 and 500 MHz for ^{1}H and 100 and 125 MHz for ^{13}C. Mass spectrometry was performed using a magnetic sector instrument by fast atom bombardment (FAB) using the indicated matrix. The matrix "magic bullet" is a 5:1 (w:w) mixture of dithiothreitol:dithioerythritol.

Details of the X-ray crystallographic structure determination of 3C.

A colorless rod with dimensions 0.545 x 0.182 x 0.182mm^3 was placed and optically centered on the CCD system at –120°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω scans (25 frames/series) that were well distributed in reciprocal space. Data frames were collected [MoKα] with 0.3° wide ω-scans, 90 seconds per frame, 606 frames per series. Five complete series were collected, at varying φ angles (φ=0°, 72°, 144°, 216°, 288°) with an additional 200 frames being a repeat of the first series for redundancy and decay purposes, with a crystal to detector distance of 4.950cm, thus providing a complete sphere of data to $2\theta_{max}$=55.0°. A total of 100707 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS[1,2] with 5022 unique [R(int)=0.0274].

Structural determination and Refinement:

All crystallographic calculations were performed on a Personal computer (PC) with dual Pentium 450MHz processors and 384MB of extended memory. The SHELXTL[3] program package was now implemented, XPREP, to determine the probable space group and set up the initial files. System symmetry and systematic absences clearly indicated the centrosymmetric rhombohedral space group R-3 (no. 148). The 100707 data collected were merged based upon identical indices yielding 70020 data [R(int)=0.0296]. Due to the inherent weakness of the data they were further truncated to $2\theta_{max}$=50.0° yielding 55632 data which were then merged, during least-squares refinement, to 9642 unique data [R(int)=0.0397]. The structure was determined by direct methods with the successful location of nearly all atoms using the program XS[4]. The structure was refined with XL[5]. After the initial refinement difference-Fourier cycle, additional atoms were located and input. All of the atoms that were fully occupied were refined isotropically, then anisotropically; those found to be disordered were refined isotropically. Additional solvent

molecules were also located; a toluene molecules was found to be disordered and refined for two orientations, a $CHCl_3$ molecule was also disordered in the chlorine positions and modeled, a water molecule was also located with its hydrogen positions placed in logical locations. A final benzene/toluene molecule was also located about a special position (-3) but the close proximity of the molecule of interest precluded logical fitting of a methyl group onto the ring atom found. All of the hydrogen atoms within all of these molecules were placed in calculated positions and allowed to ride on their parent atom. The final structure was refined to convergence [$\Delta/\sigma \leq 0.001$] with R(F)=7.72%, wR(F^2)=17.39%, GOF=1.144 for all 9642 unique reflections [R(F)=5.29%, wR(F^2)=15.79% for those 7164 data with Fo > 4σ(Fo)]. A final difference-Fourier map was featureless indicating that the final structure is therefore correct and complete.

The function minimized during the full-matrix least-squares refinement was $\Sigma w(Fo^2 - Fc^2)$ where $w=1/[\sigma^2(Fo^2)+(0.1011*P)^2+ 19.413*P]$ and $P=(max(Fo^2,0)+2*Fc^2)/3$. An empirical correction for extinction was also applied to the data in the form $(Fc^2,corr) = k[1 + 0.001 * x * Fc^2 * \lambda^3/sin(2\theta)]^{(-1/4)}$ where k=0.02931 is the overall scale factor. The value determined for x was 0.00002(3).

References:
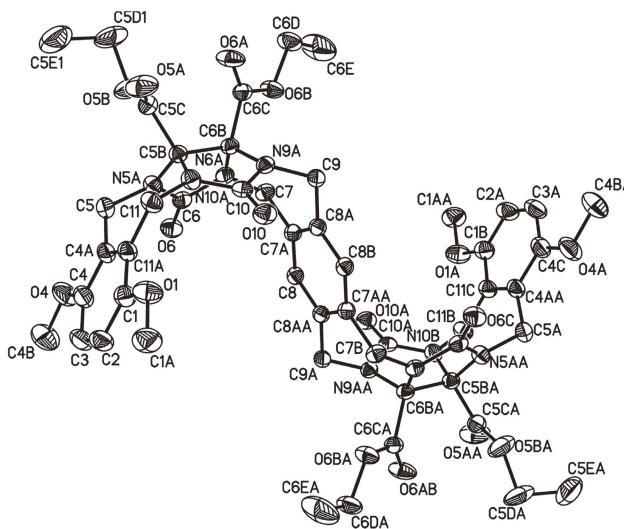
1) An Empirical Correction for Absorption Anisotropy, Blessing, R. H. (1995). Acta Cryst., A51, 33-38.

2) Sheldrick, G.M., SADABS 'Siemens Area Detector Absorption Correction' Universität Göttingen: Göttingen, Germany, 1996.

3) Sheldrick, G.M., (1994). SHELXTL/PC. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

4) Phase Annealing in SHELX-90: Direct Methods for Larger Structures, Sheldrick, G. M., (1990). Acta Cryst. A46, 467-473.

5) Sheldrick, G.M., (1993). Shelxl93 Program for the Refinement of Crystal Structures. University of Göttingen, Germany.

6) On Enantiomorph-Polarity Estimation, Flack, H.D. (1983). Acta Cryst., A39, 876-881.

Table 1. Crystal data and structure refinement for [C50H54N8O16].

Identification code	525ffmi
Empirical formula	C57.56 H63 Cl0.67 N8 O16.22
Formula weight	1150.02
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system	Rhombohedral
Space group	R-3

Unit cell dimensions

$a = 47.427(5)$ Å	$\alpha = 90°$.
$b = 47.427(5)$ Å	$\beta = 90°$.
$c = 12.6667(18)$ Å	$\gamma = 120°$.

Volume	24674(5) Å^3
Z	18
Density (calculated)	1.393 Mg/m^3
Absorption coefficient	0.134 mm^{-1}
F(000)	10898
Crystal size	0.545 x 0.182 x 0.182 mm^3
Theta range for data collection	1.49 to 25.00°.
Index ranges	-56<=h<=56, -56<=k<=56, -15<=l<=15
Reflections collected	55632
Independent reflections	9642 [R(int) = 0.0397]
Completeness to theta = 25.00°	99.9 %
Absorption correction	Empirical, SADABS
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9642 / 12 / 779
Goodness-of-fit on F^2	1.144
Final R indices [I>2sigma(I)]	R1 = 0.0529, wR2 = 0.1579 [7164 Data]
R indices (all data)	R1 = 0.0772, wR2 = 0.1739
Extinction coefficient	0.00002(3)
Largest diff. peak and hole	0.762 and -0.579 e.Å^{-3}

Details of the X-ray crystallographic structure determination of 3S.

A colorless block with approximate orthogonal dimensions 0.375 x 0.220 x 0.163mm^3 was placed and optically centered on the CCD system at –80°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω-scans, 10 seconds per frame, and 25 frames per series that were well distributed in reciprocal space. Data frames were collected [MoKα] with 0.3° wide ω-scans, 20 seconds per frame and 606 frames per series. Five complete series were collected at varying φ angles (φ=0°, 72°, 144°, 216°, 288°). An additional 200 frames, a repeat of the first series for redundancy and decay purposes, were also collected. The crystal to detector distance was 4.843cm, thus providing a complete sphere of data to $2\theta_{max}$=55.0°. A total of 22317 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS[1,2] with 6366 unique [R(int)=0.0205]

Structural determination and Refinement:

All crystallographic calculations were performed on a Personal computer (PC) with a Pentium 1.80GHz processor and 512MB of extended memory. The SHELXTL[3] program package was implemented, XPREP, to determine the probable space group and set up the initial files. Lack of system symmetry, no systematic absences and intensity statistics indicated the unique centrosymmetric triclinic space group P-1 (no. 2). The structure was determined by direct methods with the successful location of nearly all non-hydrogen atoms using the program XS[4]. The structure was refined with XL[5]. After one refinement cycle, all of the remaining full occupancy non-hydrogen atoms were located. Additional least-square difference-Fourier cycles revealed disorder in multiple locations that were individually modeled and optimized. All of the non-hydrogen atoms were allowed to refine anisotropically. Hydrogen atoms were initially calculated and placed in idealized positions and those fully occupied later allowed to refine freely. Partial occupancy carbon atoms with attached hydrogen atoms were placed in calculated idealized positions throughout. The final structure was refined to convergence [$\Delta/\sigma \leq 0.001$] with R(F)=5.41%, wR(F^2)=13.09%, GOF=1.107 for all 6366 unique reflections [R(F)=4.44%, wR(F^2)=12.45% for those 5288 data with Fo > 4σ(Fo)]. The final difference-Fourier map was essentially featureless, indicating that the structure is both correct and complete.

The function minimized during the full-matrix least-squares refinement was $\Sigma w(Fo^2-Fc^2)$ where w=1/[$\sigma^2(Fo^2)$+(0.0727*P)^2+0.3349*P] and P=(max(Fo^2,0)+2*Fc^2)/3. An empirical correction for extinction was also applied to the data in the form (Fc^2,corr) = k[1 + 0.001 * x * Fc^2 *

$\lambda^3/\sin(2\theta)]^{(-1/4)}$ where k=0.19498 is the overall scale factor. The value determined for x was 0.0021(17).

References:

1) An Empirical Correction for Absorption Anisotropy, Blessing, R. H. (1995). Acta Cryst., A51, 33-38.

2) Sheldrick, G.M., SADABS 'Siemens Area Detector Absorption Correction' Universität Göttingen: Göttingen, Germany, 1996.

3) Sheldrick, G.M., (1994). SHELXTL/PC. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

4) Phase Annealing in SHELX-90: Direct Methods for Larger Structures, Sheldrick, G. M., (1990). Acta Cryst. A46, 467-473.

5) Sheldrick, G.M., (1993). Shelxl93 Program for the Refinement of Crystal Structures. University of Göttingen, Germany.

Table 1. Crystal data and structure refinement for [C26H29N4O8Cl2].

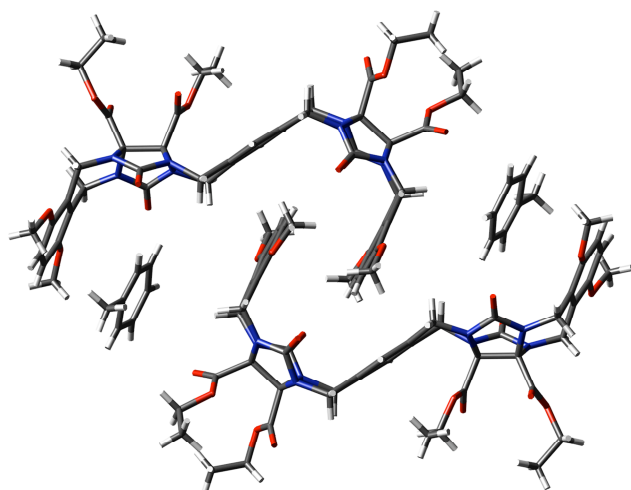|	
Identification code	816ff
Empirical formula	C26 H29 Cl2 N4 O8
Formula weight	596.43
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 10.5291(7) Å α= 87.8560(10)°.
	b = 10.7853(8) Å β= 89.7060(10)°.
	c = 12.3102(8) Å γ = 84.6100(10)°.
Volume	1390.78(17) Å^3
Z	2
Density (calculated)	1.424 Mg/m^3
Absorption coefficient	0.289 mm^{-1}
F(000)	622
Crystal size	0.375 x 0.220 x 0.163 mm^3
Theta range for data collection	1.94 to 27.50°.
Index ranges	-13<=h<=13, -13<=k<=14, -15<=l<=15
Reflections collected	22317
Independent reflections	6366 [R(int) = 0.0205]
Completeness to theta = 27.50°	99.6 %
Absorption correction	Empirical, SADABS
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6366 / 0 / 497
Goodness-of-fit on F^2	1.107
Final R indices [I>2sigma(I)]	R1 = 0.0444, wR2 = 0.1245 [5288 Data]
R indices (all data)	R1 = 0.0541, wR2 = 0.1309
Extinction coefficient	0.0021(17)
Largest diff. peak and hole	0.392 and -0.466 e.Å^{-3}

Figure S1. Illustration of the dimeric packing of **3C**•2PhCH$_3$ in the crystal.
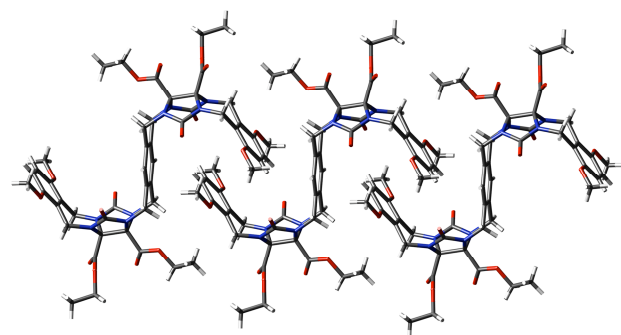

Figure S2. Illustration of the infinite tape-like motif formed by **3S** in the crystal.

Self-Association and 1:1 Binding Models Used in Scientist. All calculations were performed on a personal computer running Scientist.

Model used to calculate the self-association constants given in the text:

```
// MicroMath Scientist Model File
IndVars: Atot
DepVars: Deltaobsa, Deltaobsb, Deltaobsc, Deltaobsd, Deltaobse
Params: Deltazeroa, Deltasata, Deltasatb, Deltazerob, Deltasatc, Deltazeroc, Deltasatd,
Deltazerod, Deltasate, Deltazeroe, Keq
Keq = Adimer / Amono^2
Atot=Amono+2*Adimer
Deltaobsa=Deltazeroa + (Deltasata-Deltazeroa)*((2*Adimer)/Atot)
Deltaobsb=Deltazerob + (Deltasatb-Deltazerob)*((2*Adimer)/Atot)
Deltaobsc=Deltazeroc + (Deltasatc-Deltazeroc)*((2*Adimer)/Atot)
Deltaobsd=Deltazerod + (Deltasatd-Deltazerod)*((2*Adimer)/Atot)
Deltaobse=Deltazeroe + (Deltasate-Deltazeroe)*((2*Adimer)/Atot)
//Parameter Values
Deltazeroa=5.7
Deltazerob=4.7
Deltazeroc=5.1
Deltasata=5.5
Deltasatb=4.9
Deltasatc=4.9
Deltazerod=4.9
Deltasatd=4.6
Deltazeroe=4.9
Deltasate=4.6
Keq=2000
0<Adimer<0.5*Atot
0<Amono<Atot
***
```

Model used to calculate the binding constants given in Table 1 and the text:

```
// MicroMath Scientist Model File
IndVars: Xtot
DepVars: Deltaobsa, Deltaobsb, Deltaobsc, Deltaobsd, Deltaobse, Deltaobsf, Deltaobsg
Params: Deltasata, Deltazeroa, Deltasatb, Deltazerob, Deltasatc, Deltazeroc, Deltasatd,
Deltazerod, Deltasate, Deltazeroe, Deltasatf, Deltazerof, Deltasatg, Deltazerog, Keq
Keq=(Xtot-X)/(Amono*X)
Xtot=X+AX
0.0001=Amono + AX
Deltaobsa=Deltazeroa + ((Deltasata-Deltazeroa)*(AX/0.0001))
Deltaobsb=Deltazerob + ((Deltasatb-Deltazerob)*(AX/0.0001))
Deltaobsc=Deltazeroc + ((Deltasatc-Deltazeroc)*(AX/0.0001))
```

Deltaobsd=Deltazerod + ((Deltasatd-Deltazerod)*(AX/0.0001))
Deltaobse=Deltazeroe + ((Deltasate-Deltazeroe)*(AX/0.0001))
Deltaobsf=Deltazerof + ((Deltasatf-Deltazerof)*(AX/0.0001))
Deltaobsg=Deltazerog + ((Deltasatg-Deltazerog)*(AX/0.0001))
//Parameter Values
Deltasata=3.9
Deltazeroa=3.6
Deltasatb=7.0
Deltazerob=6.7
Deltasatc=5.4
Deltazeroc=5.1
Deltasatd=4.0
Deltazerod=4.1
Deltasate=4.6
Deltazeroe=4.5
Deltasatf=4.4
Deltazerof=4.3
Deltasatg=7.3
Deltazerog=7.1
Keq=2000
0<AX<0.0001
0<X<Xtot
0<Amono<0.0001
***

S11

ppm

3.557
3.883
3.923
4.190
4.230
4.380
4.421
4.656
5.066
5.107
6.657
7.007

OMe OMe

O N N O

R

R

O N N O

R = CO$_2$H

OMe OMe

13.033
4.085
4.085
4.097
4.452
4.090
2.000

Integral ppm

0 1 2 3 4 5 6 7 8 9