Supplementary Material (ESI) for Chemical Communications

Supplementary Information

A latent photoreaction predominates within water soluble calixarenes: Photochemistry of benzoin alkyl ethers

Raja Kaliappan, Lakshmi S. Kaanumalle and V. Ramamurthy*

Department of chemistry, University of Miami, Coral Gables, Florida- 33124, USA

Supplementary Material (ESI) for Chemical Communications

Experimental Protocol:

The benzoin alkyl ethers (**3a-c**) are sparingly soluble in water. For complex preparation, the required equivalents of the guest was added to an aqueous solution of the host and stirred for 6 hours. The complex formation was confirmed by ^{1}H NMR. The pH of the solution was ~ 7.7. The complexes were irradiated for ~ 10 minutes using a 450W medium pressure mercury arc lamp. The photoproducts were extracted with ethyl acetate. A known amount of benzophenone was added as an internal standard before GC analysis. The mass balance was 65-70% excluding benzaldehyde. Photoproducts were analysed by HP 5890 series-II GC using an SE-30 capillary column, error limit ± 3%.

Determination of host-guest association constants:[1]

The association constants were calculated for the following equilibrium,

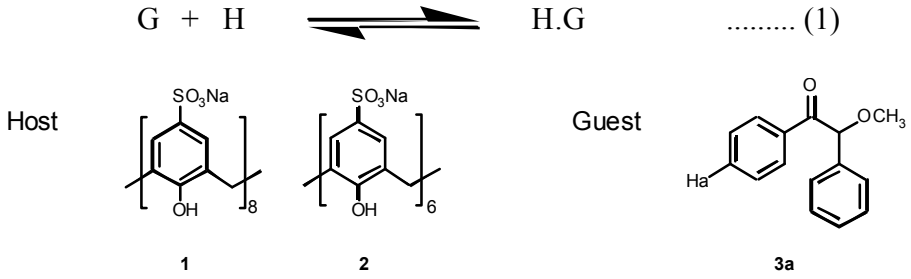


Figure S1. Structures of host **1** and **2** and guest **3a**.

Binding of benzoin methyl ether with hosts **1** and **2** was fast on the NMR time scale (400 MHz) and the determination of *K* required titration studies. The shift of the aromatic proton (H_a) signals of benzoin methyl ether (Figure S1) was recorded after each addition (~1.7 mg, 1.02×10^{-6} moles) of the host. The plot of $1/\Delta$ vs 1/[Host] is shown in Figure S2.

K according to equation (1) is given by

$$K = [H.G]/[H][G]$$

$$1/\Delta = 1/(\Delta_{11}K[H]) + 1/(\Delta_{11})$$

Where,

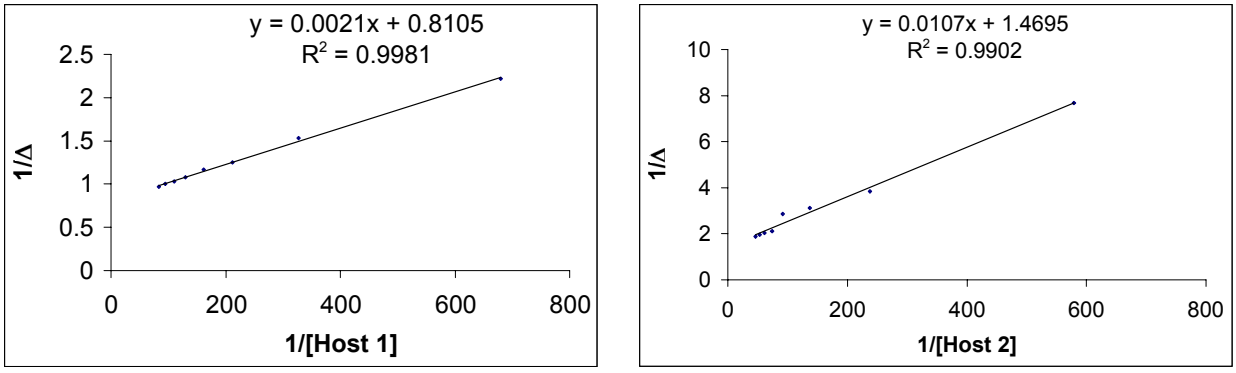
K = association constant,

$\Delta = \delta - \delta_{guest}$ and $\Delta_{11} = \delta_{complex} - \delta_{guest}$

the observed chemical shift δ is the average of the chemical shifts of the guest and the complex, $\delta_{complex}$ is the chemical shift of the complex, δ_{guest} is the chemical shift of the guest and

[H] = concentration of host.

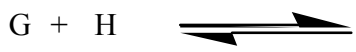
For host **1**(with guest **3a**), *K* = 386 M^{-1}, and for host **2** (with guest **3a**), *K* = 137 M^{-1}



(a) **(b)**

Figure S2. **(a)** Plot of 1/Δ vs 1/[Host **1**] **(b)** Plot of 1/Δ vs 1/[Host **2**].

Determination of the concentration of H.G complex at a given concentration of host and guest:[2]



$$K = [H.G]/[G][H]$$

$$K = [H.G] / ([G] - [H.G])([H] - [H.G])$$

$$[H.G] = 0.5[H]\{1 + R + 1/[H]K \pm ((1 + R + 1/[H]K)^2 - 4R)^{0.5}\} \quad \text{where } R = [G]/[H]$$

For complex of host **1** with guest **3a**, the values are as follows, $[G] = 3.4 \times 10^{-3}$M, $[H] = 1.2 \times 10^{-2}$M and $[H.G] = 2.6 \times 10^{-3}$M,

percentage of guest **3a** complexed to host **1** = 76

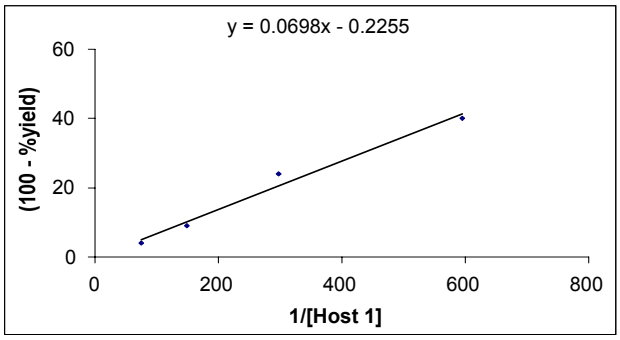
For complex of host **2** with guest **3a**, the values are as follows, $[G] = 4.76 \times 10^{-3}$M, $[H] = 2.13 \times 10^{-2}$M and $[H.G] = 3.38 \times 10^{-3}$M,

percentage of guest **3a** complexed to host **2** = 70

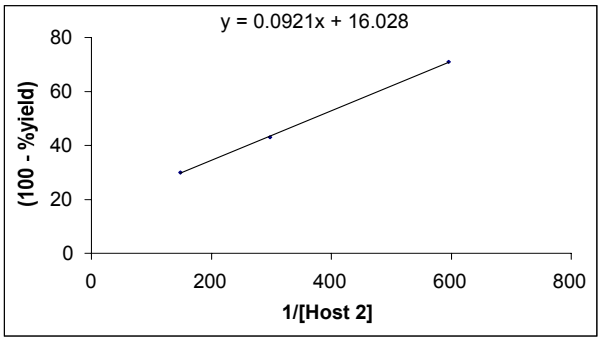
Percentage relative yield of deoxybenzoin at infinite concentration of host:

Percentage relative yields of deoxybenzoin at infinite concentration of the hosts **1** and **2** were calculated by extrapolating the plot of (100 - %yield) vs 1/[Host] as shown in Figure S3. At infinite concentration of the respective host, the percentage yield is given below,

For host **1**, percentage yield = 100 and for host **2**, percentage yield = 84



(a)



(b)

Figure S3. (a) Plot of (100 - %yield) vs 1/[Host **1**] **(b)** Plot of (100 - %yield) vs 1/[Host **2**].

References:

1. K. A. Connors, *Binding Constants. The Measurement of Molecular Complex Stability*, Wiley, New York, 1987; 189-200.

2. G. G. González and G. Tardajos, *J. Chem. Educ*., 2004, **81**, 270-274.