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A Switchable Hydrophobic Cavity of Disodium 1,8-Disulfonato-3,4,5,6-acridinetetracarboxylic Acid

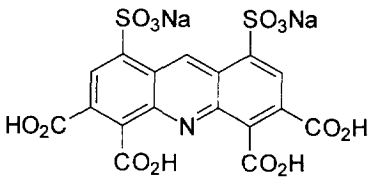
Bo-Long Poh* and Beng Chin Kang

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia.

Abstract: Disodium 1,8-disulfonato-3,4,5,6-acridinetetracarboxylic acid **1** in water forms a dimer that encloses a hydrophobic cavity. This hydrophobic cavity is switchable because, in the presence of sodium hydroxide, it disappears as a result of converting the dimer of **1** to its monomer by the base.

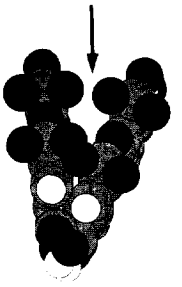
Switchable guest-binding synthetic receptor molecules are useful models of biochemical receptor molecules which bind their substrates reversibly. Several of them that bind cations have been reported[1,2]. The reversible switching mechanism is based on electrochemical, redox, photo, pH or temperature response.

We have recently shown[3] that disodium 1,8-disulfonato-3,4,5,6-acridinetetracarboxylic acid **1** exists in the dimeric form in water (the CPK molecular model of the dimer is shown in **2**) and the hydrophobic cavity enclosed by the dimer binds polyaromatic hydrocarbons strongly[4]. This paper reports that this hydrophobic cavity is switchable by pH control.



1

Hydrophobic cavity



2

We studied the binding of two polyaromatic hydrocarbons, anthracene and chrysene, by **1** in an

aqueous medium containing various concentrations of sodium hydroxide using the transport method. The rates of transport of anthracene and chrysene from one hexane phase to another through an aqueous phase containing **1** and various concentrations of sodium hydroxide in an U-tube were monitored by measuring the absorbance at a given wavelength of the two hydrocarbons in the receiving phase[5]. Figure 1 shows the plots of absorbance against time taken for chrysene to travel from the source phase to the receiving phase.

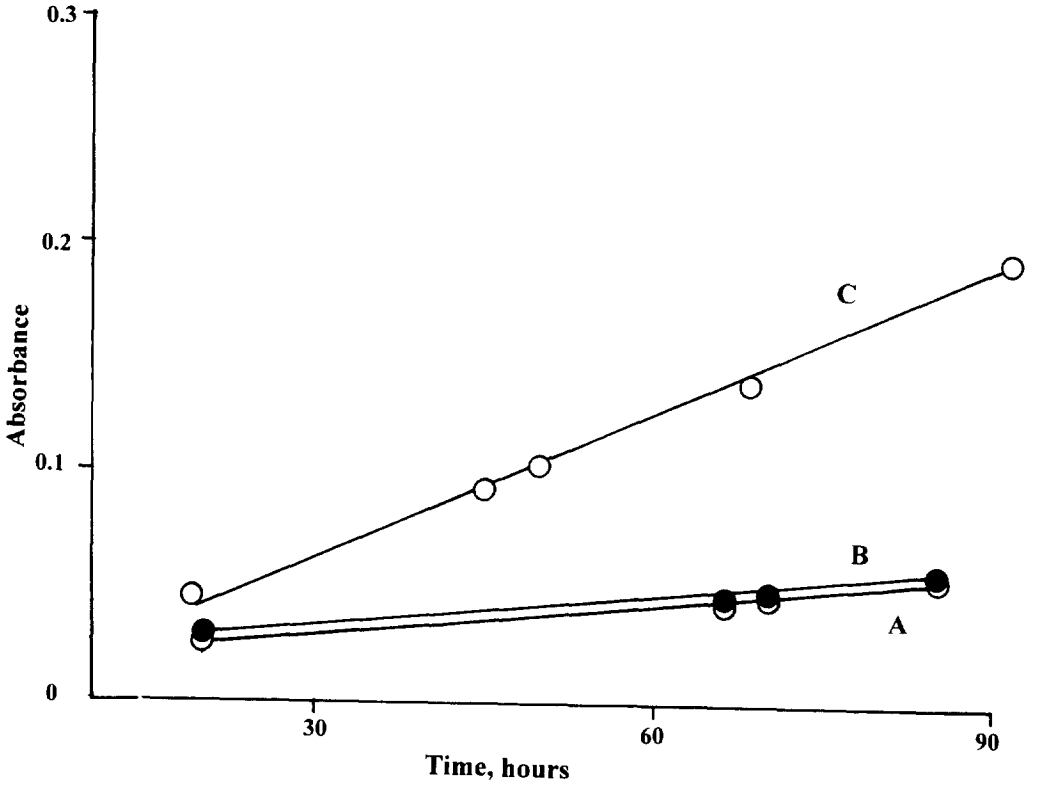


Figure 1. Relationship between absorbance at 266 nm of chrysene in the receiving phase and time. The initial concentration of chrysene in the source phase is 0.005 M; (**A**) no host in aqueous phase, (**B**) 0.002 M of **1** and 0.1 M of NaOH in the aqueous phase and (**C**) 0.002 M of **1** in the aqueous phase.

The stability constants K of the 1:1 host to guest complexes[4] formed from the inclusion of the two polyaromatic hydrocarbons inside the cavity of **2** were calculated from the slopes of such plots given in Figure 1, using the equation given earlier[5]. Figure 2 shows the plots of K values versus the concentration of sodium hydroxide present in the aqueous phase containing 0.002 M of **1**.The values of K decrease with increase in

sodium hydroxide concentration. At 0.004 M of sodium hydroxide the K values for the two polyaromatic hydrocarbons are practically zero, indicating that **1** no longer exists in the dimeric form **2** when two carboxylic groups have been ionized . The unfavourable electrostatic repulsion between the negative charges of the ionized carboxylic groups has changed the dimeric host to the monomer which has no cavity. Thus, the hydrophobic cavity present in **2** can be switched on and off by pH control.

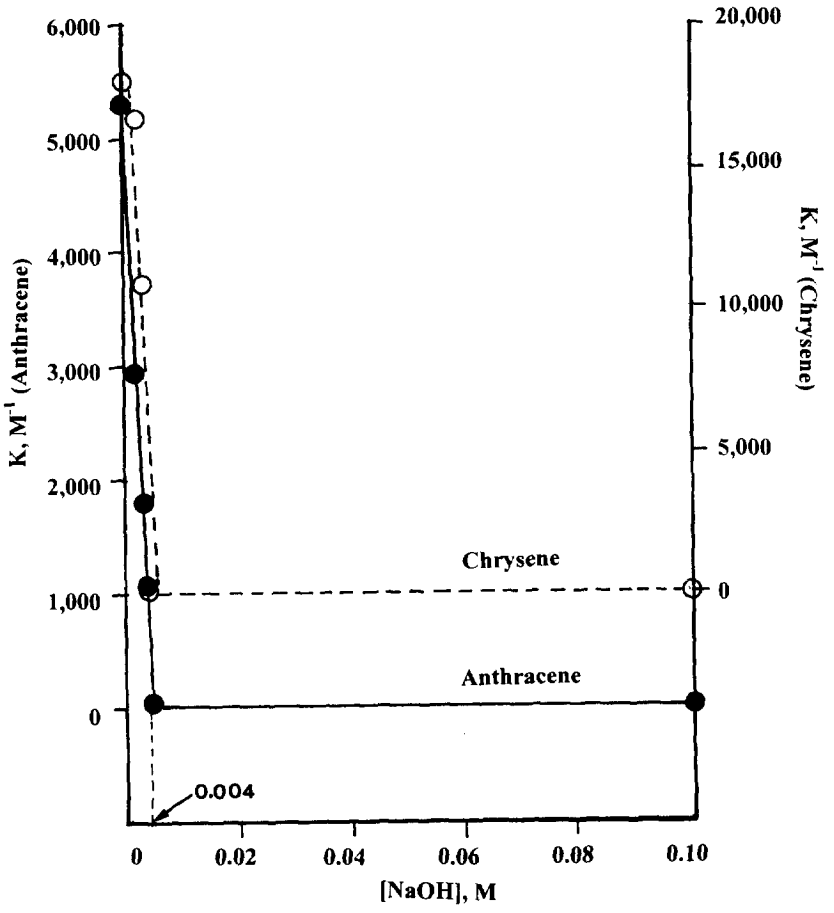


Figure 2. Relationship between stability constant K and concentration of sodium hydroxide.

EXPERIMENTAL

Materials. Anthracene and chrysene were commercial samples. They were purified by recrystallization from ethanol. The synthesis of **1** was reported earlier[3]. Previously, the orange cyclic tetramer (prepared from the reaction between H-acid and formaldehyde[6]) used in the preparation of **1** could be obtained in only about 20% yield. However, it can now be obtained in quantitative yield as follows.

To a mixture of H-acid, monosodium salt (0.85 g, 2.5 mmole) and chromotropic acid, disodium salt (0.50 g, 1.25 mmole) in 25 mL of distilled water in a round-bottom flask was added 0.20 mL of 37% formaldehyde solution (2.5 mmole). The resulting mixture was refluxed for 15 minutes. When cooled in an ice-water bath, an orange solid precipitated out. It was suctioned filtered. The sticky solid was then triturated in several portions of acetone to obtain a dry powdery solid. Drying at 70 ^{0}C in an oven for an hour removed any trace of acetone trapped in the solid. The product was of high purity, not different from a sample recrystallized from water. The yield was 0.95 g (86%). Chromotropic acid, disodium salt acted as a catalyst in the reaction; it was recovered unchanged.

Transport experiments were carried out as described before[5].

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REFERENCES

1. Izatt, R.M., Pawlak, K. and Bradshaw, J.S., *Chem. Rev.*, **1991**, *91*, 1721.
2. Shinkai, S., In *Comprehensive Supramolecular Chemistry*, ed. Gokel, G.W., vol.1, 1996, p 672, Elsevier Science Ltd., UK.
3. Poh, B.-L. and Thee, K.K., *Tetrahedron Lett.*, **1996**, *37*, 7433. A joint paper by Poh, B.-L., Thee, K.K. and Mak, Thomas, C.W. on the crystal structure of **1** will be submitted shortly to J. Chem. Crystallogr. for publication.
4. Poh, B.-L. and Thee, K.K., *Tetrahedron Lett.*, **1996**, *37*, 8451.
5. Poh, B.-L., Lim, C.S. and Koay, L.-S., *Tetrahedron*, **1990**, *46*, 6155.
6. Poh, B.-L., Chin, L.Y. and Lee, C.W., *Tetrahedron Lett.*, **1995**, *36*, 3877.

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