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# A New [2]Pseudorotaxane from 1,2-Bis(isoquinolinium)ethane Salt/Dibenzo-24-crown-8 Ether

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*A new [2]pseudorotaxane from the 1,2-bis(isoquinolinium)ethane axle and the dibenzo-24-crown-8 ether wheel and its self-assembly were investigated by $^1H$ NMR spectroscopy and single crystal X-ray diffraction technique. The results demonstrated that the supramolecular adduct was held together by three noncovalent interaction such as $N^+ \cdots O$ ion–dipole interactions, $C\text{-}H \cdots O$ hydrogen bonding, and $\pi$-stacking between electron-poor isoquinolinium rings of the axle and electron-rich catechol rings of the wheel. They, furthermore, showed that the phenyl ring as a substituent or a fused ring on pyridinium has a similar effect on the association ability.*

**Keywords** DB24C8; hydrogen-bonding; ion–dipole interaction; pseudorotaxane; $\pi$-stacking interaction

## Introduction

The interpenetrated molecules have attracted an ever-increasing interest from supramolecular scientists. They have widely been applied for the construction of supramolecular architectures with charming topological geometry. The motif of 1,2-bis(pyridinium)ethane/crown ether has originally been demonstrated by Loeb and Wisner [1–5] and further employed to construct many metal-organic rotaxane frameworks (MORFs) [6–8]. Herein, an analog 1,2-bis(isoquinolinium)ethane is shown as an axle to thread through the cavity of the dibenzo-24-crown-8 (DB24C8) ether, forming a [2]pseudorotaxane, and it further packs to form supramolecular bricklaying [9].

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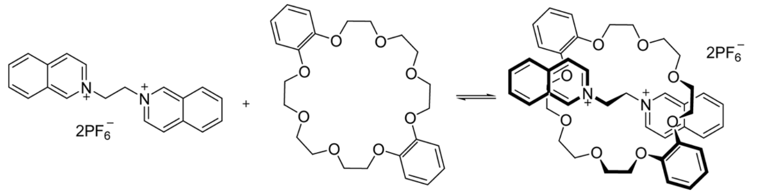

## Experimental

### *General*

Isoquinoline, 1,2-dibromoethane, and ammonium hexafluorophosphate were of reagent grade. Dibenzo-24-crown-8 (DB24C8) was purchased from Sigma-Aldrich Co. Ltd. Deuterated solvents were available from Cambridge Isotope Laboratories and used as received. All other solvents were of analytical grade and used as received. All NMR spectra were recorded at 25°C on a Varian INOVA500 spectrometer using the deuterated solvent as the lock and the residual solvent as the internal reference. Determination of the unit cell and data collection were performed on a Bruker Smart 1000 diffractometer using graphite monochromated Mo $K_\alpha$ radiation.

### *Preparation of 1,2-Bis(isoquinolinium)ethane Hexafluorophosphate*

The axle 1,2-bis(isoquinolinium)ethane salt was prepared by a modified literature method [1]. A solution of isoquinoline (3.87 g, 30 mmol) in DMF (5 mL) was preheated to 80°C, followed by dropwise addition of a dilute DMF (10 mL) solution of 1,2-dibromoethane (1.88 g, 10 mmol) over 4 h. After addition, the reaction continued over a 3-d period and gradually cooled to room temperature. The resulting precipitate was filtered, washed with anhydrous diethyl ether (3 × 20 mL), and dried under vacuum. Recrystallization from distilled water provided brick-like red crystals (0.47 g, 1.1 mmol) in a 11% yield. $^1$H NMR (500 MHz, $D_2O$) $\delta$ 9.55 (s, 2 H, $^1$CH), 8.35–8.32 (m, 4 H, $H_{arom}$), 8.18–8.13 (m, 6 H, $H_{arom}$), 7.93–7.90 (m, 2 H, $H_{arom}$), 5.43 (s, 4 H, $CH_2$-$N^+$); $^{13}$C NMR (125 MHz, $D_2O$) $\delta$ 150.09 (2C), 138.54 (2C), 138.22 (2C), 133.86 (2C), 132.31 (2C), 130.48 (2C), 127.95 (2C), 127.70 (2C), 127.68 (2C), 60.38 (2C). The obtained Br salt (0.81 g, 5.0 mmol) was dissolved in hot water (1 mL), and saturated aqueous $NH_4PF_6$ (1 mL) was added, resulting in a white precipitate. The mixture was allowed to cool slowly to room temperature and the white powder produced isolated by filtration. The yield of $PF_6$ salt was 0.20 g (74%). $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 9.51 (s, 2 H, $^1$CH), 8.44 (d, $J = 6.8$ Hz, Hz, 2 H, $H_{arom}$), 8.38 (dd, $J_1 = 8.5$ Hz, $J_2 = 1.0$ Hz, 2 H, $H_{arom}$), 8.32–8.27 (m, 6 H, $H_{arom}$), 8.10–8.06 (m, 2 H, $H_{arom}$), 5.30 (s, 4 H, $CH_2$-$N^+$).

### *Preparation of [2]Pseudorotaxane Crystals*

The $PF_6$ salt and DB24C8 were dissolved in acetonitrile (0.5 mL), respectively. Both the solutions were combined to form a light-yellow solution. It was allowed to stand at room temperature over about one week, and [2]pseudorotaxane was obtained as light-yellow crystals, confirmed by X-ray single crystal diffraction and $^1$H NMR spectrum.

## Results and Discussion

### *Crystal Study*

The DB24C8 complex of the 1,2-bis(isoquinolinium)ethane crystallized with two [2]pseudorotaxane and four acetonitrile molecules per unit cell in the monoclinic space group $P2_1/c$, requiring the solution of only half of one centrosymmetric pseudorotaxane, the rest of the cell being related by symmetry ($-x$, $-y+1$, $-z+1$) [10]. The $PF_6$ counterions were found to be disordered, responsible for the high R1 value.

In the pseudorotaxane, the 1,2-bis(isoquinolinium)ethane axle has an *anti*-conformation around the C22-C22′ center, likely due to the intramolecular repulsion of the positively charged nitrogen atoms ($d_{N-N} = 3.712$ Å), and the crown ether extends both its catechol rings with the S-shape configuration (Fig. 1). The catechol ring lies at a 5.3° interplanar angle and a ca. 3.63 Å interplanar spacing to the isoquinolinium ring, indicative of $\pi$-$\pi$ stacking interaction in this structure. The long axis of the crown is inclined to that of the thread by 29.2°, and the aryl oxygen atom (O1) is positioned over the isoquinolinium $N^+$ center. This results in the maximum ion–dipole interaction and hydrogen bonding, as was reported in the pseudorotaxane from 1,2-bis-(4-phenyl- pyridinium)ethane and DB24C8 [11].

$N^+ \cdots O$ ion–dipole stabilization is evident from several short to medium contacts between the quaternized nitrogen centers and the ether oxygen atoms ($N1 \cdots O1 = 3.446$ Å, $N1 \cdots O2 = 3.698$ Å, $N1 \cdots O3 = 3.902$ Å, $N1 \cdots O4 = 3.800$ Å, $N1 \cdots O3' = 3.913$ Å). These contributions are augmented by the presence of eight hydrogen bonds involving the central methylene and $\alpha$-isoquinolinium hydrogen atoms of the axle and

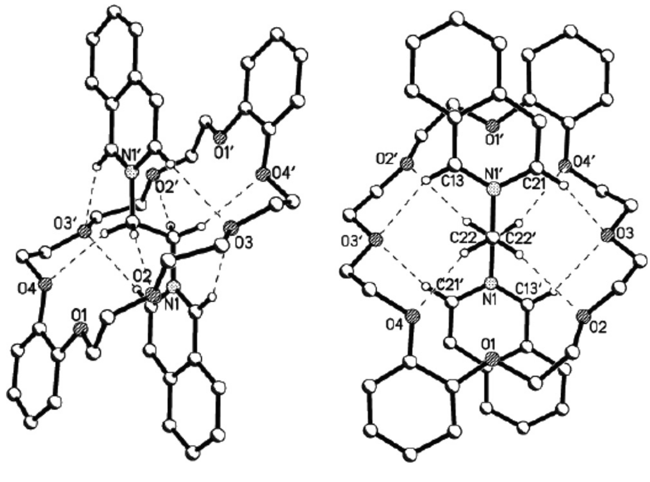

**Figure 1.** Two views of the crystal structure of the pseudorotaxane formed from the axle and DB24C8. Most of hydrogens, two acetonitrile molecules, and hexafluorophosphate counterions are omitted for clarity.

**Table 1.** Hydrogen bonding parameters in the crystal structure of pseudorotaxane

| C-H···O | H···O (Å) | C···O (Å) | C-H···O (°) |
|---|---|---|---|
| C13-H13···O3 | 2.53 | 3.395 | 155 |
| C21-H21···O3 | 2.51 | 3.335 | 148 |
| C22-H22A···O4 | 2.39 | 3.311 | 159 |
| C22-H22B···O2 | 2.55 | 3.476 | 159 |

the six oxygen atoms of the DB24C8 ether (Table 1). It is worthwhile to note that the aryl oxygen atoms display shorter H···O distances than their alkyl counterparts. This is contrary to the fact that alkyl oxygen atoms with greater basicity generally display shorter intramolecular contacts, and also is different from those reported by Wisner [12].

From the analysis above, the relative orientation of the axle and the wheel mainly results from the $N^+\cdots O$ ion–dipole interactions, reinforced by C···O hydrogen bonding and π-stacking.

Expectedly, no complex hydrogen-bonding network or linear tape occurs in the spatial packing of this [2]pseudorotaxane, most probably due to the absence of good hydrogen-bonding acceptors or donors in itself. However, pseudorotaxane sheets are constructed by the aid of acetonitrile molecules and counterions. π-π interactions (with interplanar angle of 5.42° and interplanar spacing of 3.323 Å) between adjacent sheets facilitate to form supramolecular walls (Fig. 2) using the pseudorotaxane as brick, just like the real wall in our life.

Evidently, the introduction of isoquinolinium ring apt to π-stacking is responsible for this supramolecular bricklaying.

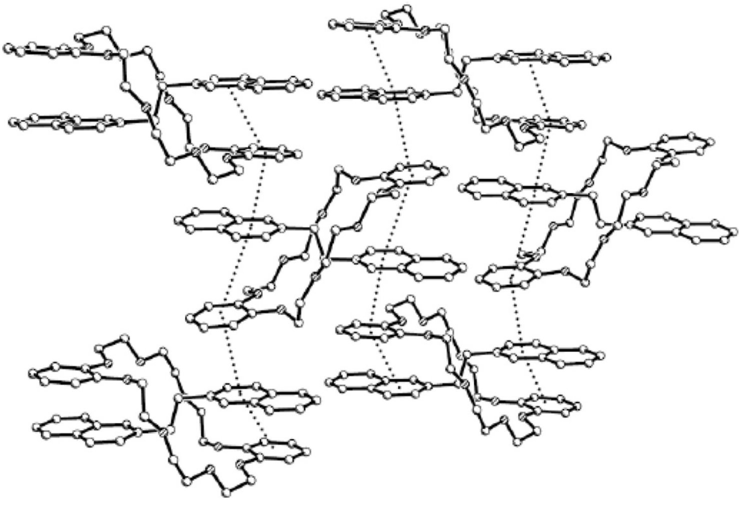

**Figure 2.** The supramolecular wall constructed by the axle$\subset$DB24C8 via π-stacking between catechol and pyridyl ring of isoquinolinium salt. The acetonitriles and counterions are omitted.

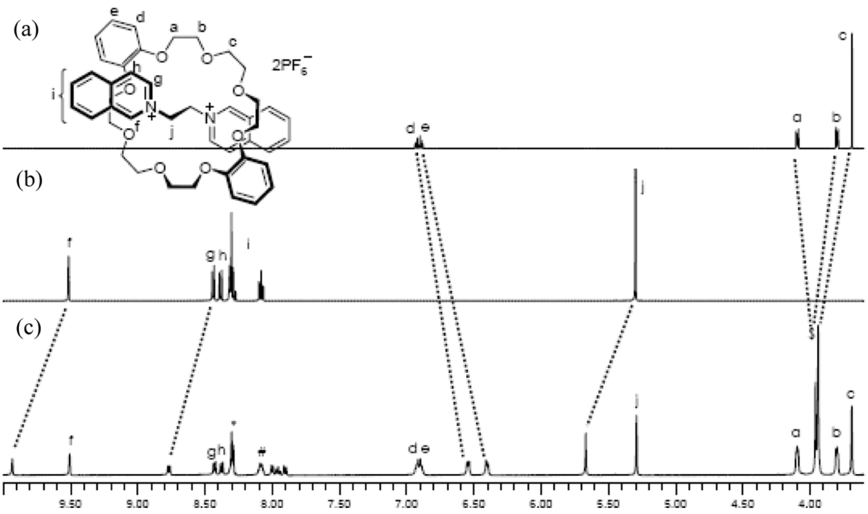

**Figure 3.** $^1$H NMR spectra of (a) free DB24C8, (b) free axle, and (c) their equimolar mixture.

### *$^1$H NMR Spectroscopy*

Analysis of the $^1$H NMR spectrum of the pseudorotaxane complex was performed in MeCN-$d_3$ due to the good solubility of both the hexafluorophosphate and DB24C8 in this solvent. An integrated spectrum of a 1:1 mixture of the dication and DB24C8, and the individuals are shown in Fig. 3.

As can be seen in Fig. 3, there are three sets of independent resonance signals at equilibrium, corresponding to the free axle, free crown ether, and the complex, respectively. This suggests that the rate of association and dissociation is slow with respect to the NMR scale. After association, the chemical shifts of central methylene protons ($H_j$, $\Delta\delta = 0.378$ ppm) and $\alpha$-isoquinolinium protons ($H_f$, $\Delta\delta = 0.427$, and $H_g$, $\Delta\delta = 0.339$ ppm) on the axle moved downfield. This downshift is characteristic of the existence of C-H$\cdots$O hydrogen bonding between the axle and DB24C8. The resonances of the other protons on isoquinolinium rings and all protons ($H_d$ and $H_e$) on catechol rings moved upfield. This results from the $\pi$-stacking between the host and guest moieties. Besides, $\alpha$-ethyleneoxyl protons $H_a$ shifted upfield, while $\beta$-ethyleneoxyl protons $H_b$ and $\gamma$-ethyleneoxyl protons $H_c$ shifted downfield. The typical chemical shifts of protons on the axle and DB24C8, and the corresponding changes are shown in Table 2.

### *Determination of Associate Constant*

As mentioned above, signals for the complexed and uncomplexed species are observed (Fig. 3c). Since absolute concentrations can be deduced readily from the relative abundances of the three species at equilibrium when the initial concentrations of both the axle and DB24C8 are known, single point determination of the association constant ($K_a$) is possible. As for this pseudorotaxane, if the integrals for the central methylene protons of the complexed ($\delta = 5.668$ ppm) and uncomplexed ($\delta = 5.291$ ppm) thread are 1 and 1.2, respectively, and the initial

**Table 2.** The typical chemical shifts ($\delta$) of the axle, DB24C8 and their equimolar mixture, and the corresponding changes

| | axle | DB24C8 | axle $\subset$DB24C8 | |
|---|---|---|---|---|
| | $\delta$ | $\delta$ | $\delta$ | $\Delta\delta$ |
| Hf | 9.506 (s) | | 9.933 (s) | 0.427 |
| Hg | 8.428 (d) | | 8.767 (s) | 0.339 |
| Hh | 8.376 (d) | | 8.302–8.272 (m) | |
| Hi | 8.318–8.271 (m) | | 8.103–8.063 (m) | |
| | | | 7.999 (d) | |
| | | | 7.956 (t) | |
| | 8.097–8.063 (m) | | 7.903 (d) | |
| Hd | | 6.916 (m) | 6.543 (dd) | |
| He | | 6.899 (m) | 6.402 (dd) | |
| Hj | 5.291 (s) | | 5.669 (s) | 0.378 |
| Ha | | 4.097 (m) | 3.960 (s) | |
| Hb | | 3.801 (m) | 3.941 (s) | |
| Hc | | 3.691 (s) | | |

concentrations of thread and crown are $5 \times 10^{-3}$ M, then:

$$\mathrm{K}a = \frac{[\text{Thread} \subset \text{Crown}]}{[\text{Thread}][\text{Crown}]} = \frac{\frac{1}{2.2} \times 5 \times 10^{-3}\mathrm{M}}{\left(\frac{1.2}{2.2} \times 5 \times 10^{-3}\mathrm{M}\right)^2} = 306\mathrm{M}^{-1}.$$

The association constant of this pseudorotaxane comes closely to that (320 $\mathrm{M}^{-1}$) for the [2]pseudorotaxane reported previously [11], in which the thread is 1,2-bis(4-phenylpyridinium)ethane. This indicates that whether the phenyl group acts as a substituent or a fused ring at pyridinium has a similar effect on the DB24C8 complexation ability.

## Conclusions

We have presented the formation of [2]pseudorotaxane from the 1,2-bis(isoquinolinium)ethane axle and the dibenzo-24-crown ether wheel. Both solution and solid state evidence unambiquously demonstrate that this interlocked complex is held together by $\mathrm{N}^+ \cdots \mathrm{O}$ ion-dipole interactions, $\mathrm{C\text{-}H} \cdots \mathrm{O}$ hydrogen bonding, and $\pi$-stacking between electron-deficient isoquinolinium rings of the axle and electron-rich catechol rings of the wheel. Preliminary results showed that the phenyl ring as a substituent or a fused ring on pyridinium has a similar effect on the association ability. Furthermore, the supramolecular adduct has been demonstrated to construct a supramolecular wall in the solid state.

## Supplementary Data

CCDC 682513 contains the supplementary crystallographic data for this article. Copies of the data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

## References

[1] Loeb, S. J., & Wisner, J. A. (1998). *Angew Chem. Int. Ed. Engl.*, *37*, 2838–2840.
[2] Loeb, S. J., & Wisner, J. A. (1998). *Chem. Commun.*, *34*, 2757–2758.
[3] Loeb, S. J., & Wisner, J. A. (2000). *Chem. Commun.*, *36*, 845–846.
[4] Davidson, G. J. E., Loeb, S. J., Passaniti, P., Silvi, S., & Credi, A. (2006). *Chem. Eur. J.*, *12*, 3233–3242.
[5] Loeb, S. J., Tiburcio, J., & Vella, S. J. (2006). *Chem. Commun.*, *42*, 1598–1600.
[6] Davidson, G. J. E., & Loeb, S. J. (2003). *Angew Chem. Int. Ed. Engl.*, *42*, 74–77.
[7] Hoffart, D. J., & Loeb, S. J. (2005). *Angew Chem. Int. Ed. Engl.*, *44*, 901–904.
[8] Loeb, S. J. (2005). *Chem. Commun.*, *41*, 1511–1518.
[9] Matthews, C. J., Broughton, V., Bernardinelli, G., Melich, X., Brand, G., Willis, A. C., & Williams, A. F. (2003). *New. J. Chem.*, *27*, 354–358.
[10] Loeb, S. J., Tiburcio, J., & Wisner, J. A. (2006). *Org. Biomol. Chem.*, *4*, 667–680.
[11] Wisner, J. A. (1999). *Interpenetrated and interlocked molecules via bis(pyridinium) ethanes*. Dissertation for Ph.D., the University of Windsor.