

Synthesis and electrochemical properties of bis([2.2]metacyclophane) bipyridinium

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Bis([2.2]metacyclophane) bipyridinium was synthesized for the first time and it was found that this cyclophane compound was reduced at more negative potentials than the corresponding bipyridinium, having no cyclophane skeleton, due to a transannular CH– π interaction between the aromatic ring of the cyclophane and CH portion next to nitrogen atom.

Keywords: bis([2.2]metacyclophane) bipyridinium

In the past decade non-covalent binding forces such as cation– π^1 , π – π^2 and CH– π^3 interactions have been recognised as an important subject in supramolecular chemistry of a biological context. The knowledge of the energetic and stereochemical characteristics of these non-covalent interactions within defined molecular structure should allow the design of artificial molecular components that form supramolecular structures.

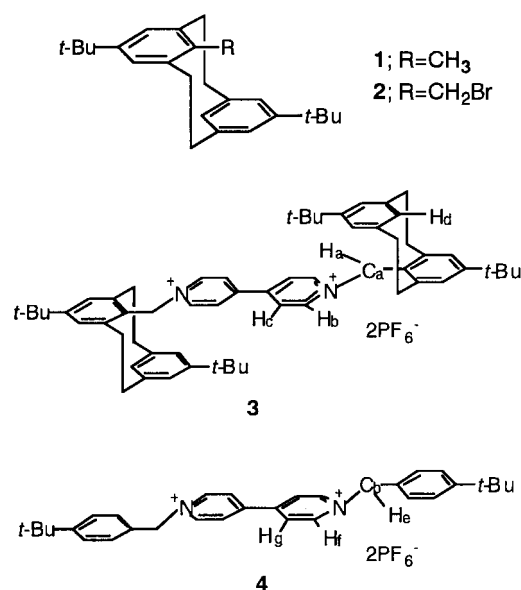
Cyclophanes, especially macrocyclic ones, have provided the model compound for research concerning the properties of such intermolecular weak interactions when they recognize the guest molecule.⁴ On the other hand, such molecular recognition cannot be expected for rigid small-sized cyclic compounds, however, they could be good candidates for investigating non-covalent weak interactions since some relevant functional groups can be fixed in defined proximity in these molecules.

We have already disclosed⁵ various unique characteristics of small-sized cyclophanes such as [2.2]metacyclophanes, which are closely related to transannular π – π interaction between two aromatic rings. In the course of our intensive investigation on this subject, [2.2]metacyclophane containing an electrochemically active moiety has been proposed, since monitoring the redox change must be a powerful tool for detecting the perturbation of the π -electronic state in the small-sized cyclophane system. The bis-quaternary salt of the bipyridinium dication has been established as the primitive prototypical electron mediator in the fields of electrochemical⁶ and photochemical⁷ applications.

Thus, here we describe the synthesis of bis([2.2]metacyclophane) bipyridinium and examine its electrochemical properties in terms of transannular CH– π interaction.

[2.2]Metacyclophane **1** was prepared according to the reported method.⁸ Bromination of **1** was carried out with NBS to give the corresponding bromomethyl compound **2**.⁹ Reaction of **2** and bipyridine in MeCN over four days afforded, after counterion exchange by NH_4PF_6 , the desired bis([2.2]metacyclophane) bipyridinium **3**. The reference compound **4** was obtained by the similar method. The compounds prepared here were characterised by NMR and MS spectroscopies and by elemental analysis.

Partial ^1H NMR spectra for the cyclophane bipyridinium **3** are summarised together with the compound **4** in Table 1. The benzyl protons (Ha) in **3** exhibit a large upfield shift compared



Scheme 1

to those in **4**, which indicates that these protons are located exclusively inside the π -cavity of the aromatic ring of the cyclophane framework, thus suffering a strong shielding effect. Although the chemical shifts of the aromatic protons (Hb and Hc) at the α - and β -positions with respect to the nitrogen atom in **3** also appear in the upfield region compared to those in **4**, this upfield shift is much smaller than that for the benzyl protons. The large upfield shift of the inner aromatic proton (Hd) was observed due to the shielding effect of the opposite aromatic ring.

Cyclic voltammetry of the bipyridinium **3** and **4** under uniform conditions in acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte at 20 °C shows two reversible reduction processes. The

Table 1 Partial ^1H NMR spectra^a of **3** and **4**

Compd	Ha/He	Chemical shift(δ)		
		Hb/Hf	Hc/Hg	Hd
3	3.86	8.18 (d, $J=7.6$)	8.01 (d, $J=7.6$)	3.79
4	5.78	8.95 (d, $J=7.2$)	8.34 (d, $J=7.2$)	–

^aIn CDCl_3 at 27 °C.

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† This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 2 Redox potentials of **3** and **4**

Compd	First couple		Second couple	
	E_p^C (V)	E_p^A (V)	E_p^C (V)	E_p^A (V)
3	-0.495	-0.388	-0.962	-0.770
4	-0.479	-0.385	-0.880	-0.780

^aBy cyclic voltametry of 1.0×10^{-3} M solutions containing 0.1 M TBAP at 50 mV s⁻¹ at 20 °C. E_p^C : cathodic potential E_p^A : anodic potential.

values of the cathodic and anodic peak potentials are summarised as E_p^C and E_p^A , respectively, in Table 2. The first one-electron reduction occurs at -0.495 V and -0.479 V in **3** and **4**, respectively. A similar difference in the potential can be seen for the second two-electron reduction. It is apparent from these results that **3** is reduced at more negative potentials, implying that the electronic state of the bipyridinium unit could be affected by the cyclophane structure.

The geometry of the cyclophane bipyridinium cation should be taken into account to explore what effects are responsible for its electronic state. However, unfortunately no crystal of the cyclophane bipyridinium salt suitable for X-ray crystallography could be obtained in spite of repeated trials. Thus, in order to obtain information about the geometry semiempirical PM3 calculations¹⁰ were conducted for **3** and **4**.

The characteristic features of compound **3** are shown in Fig. 1. These calculations also provided the energy of the LUMO level. The energy level of the LUMO in **4** was -8.4541 eV. The elevation of the LUMO level to -8.2048 eV was confirmed for **3**. This result is consistent with the reduction at more negative potentials in **3** than **4**.

It has been indicated¹¹ that a π - π stacking interaction between the bipyridinium unit and the π -electron-rich aromatic ring contributes to the reduction behavior at more negative potentials. Such a cation- π interaction is supposed to work most effectively when the face-to-face arrangement is assumed.

Considering the optimized structure of **3** as shown in Fig. 1, however, no direct interaction of bipyridinium cations and aromatic ring of the cyclophane could be expected. Taking into account into the chemical shift data and the optimized

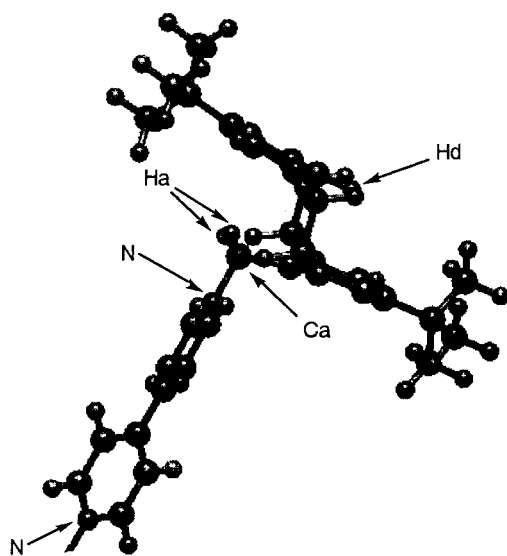


Fig. 1 Computer-generated model of **3** (One-cyclophane unit was omitted)

structure of **3**, the protons (Ha) are obviously located in the π -cavity of the opposite aromatic ring of the cyclophane. Furthermore, Ca-Ha bonding is directed toward the aromatic ring. The calculated electron densities on Ca and Ha atoms in **3** are -0.137 and +0.140, respectively. On the other hand -0.066 and +0.109 are given for Cb and He in **4**, respectively. This result could be explained by the CH- π interaction between the aromatic π -donor and C-H bonding. The existence of such an interaction can also be supported by the calculated Ca-Ha bond length (1.121Å) in **3** which is slightly longer than the corresponding length (1.112Å) in **4**.

From these results it can be suggested that the bipyridinium unit located between two [2.2]metacyclophane frameworks is reduced at more negative potentials as a result of the CH- π interaction.

This study is the first investigation of electrochemical properties in the [2.2]metacyclophane framework from the viewpoint of specific transannular interaction. It has been revealed that the reduction of the bipyridinium unit incorporated into the [2.2]metacyclophane framework takes place at more negative potentials than the referential bipyridinium. This result can be explained by the existence of the weak transannular interaction between C-H bonding neighbouring with the nitrogen atom and the opposite aromatic ring in [2.2]metacyclophane. It is noted that such a CH- π interaction clearly has an effect on the chemical properties of small-sized cyclophane compounds.

Experimental

All melting points are uncorrected. ¹H NMR spectra were recorded at 500 MHz in CD₃CN with Me₄Si as internal reference. *J* values are given in Hz. FABMS spectra were obtained on samples in a glycerol matrix using 6 KeV xenon atoms.

Bis([2.2]metacyclophane)bipyridium 3: After a solution of **2** (410 mg, 1.00 mmol) and 4,4'-bipyridine (84 mg, 0.51 mmol) in dry MeCN (25 ml) was heated under reflux for 4 days under nitrogen, the solvent was removed *in vacuo* to leave the residue. The residue was dissolved in MeCN and H₂O, and a saturated aqueous solution of NH₄PF₆ was added until no further precipitation was observed. The yellow solid was filtered off, washed with H₂O repeatedly and dried to give **3** (206 mg, 37 %) as yellow powder (MeOH): m.p. 269–271 °C; UV (EtOH) 235 nm (ϵ 18000 M⁻¹ cm⁻¹), 260 nm (ϵ 18800 M⁻¹ cm⁻¹); ¹H NMR δ 1.36 (18H, s), 1.38 (18H, s), 2.26–2.68 (8H, m), 3.08–3.17 (8H, m), 3.79 (2H, s), 3.86 (4H, s), 7.35–7.36 (8H, m), 7.92 (4H, d, *J* 6.9), 8.10 (4H, d, *J* 6.9); FABMAS *m/z* 1113(M⁺). Found: C, 64.54; H, 6.69; N, 2.46%. C₆₀H₇₄F₁₂N₂P₂ requires C, 64.74; H, 6.72; N, 2.52%.

Bis(4-tert-butylbenzyl)viologen 4: The compound (**4**) was obtained according to the procedure described for the synthesis of **3** as yellow needles (MeOH): m.p. >300 °C; UV (EtOH) 215 nm (ϵ 11000 M⁻¹ cm⁻¹), 260 nm (ϵ 11500 M⁻¹ cm⁻¹); ¹H NMR δ 1.32 (18H, s), 5.78 (2H, s), 3.86 (4H, s), 7.44 (4H, d, *J* 8.5), 7.55 (4H, d, *J* 8.5), 8.35 (4H, d, *J* 6.9), 8.94 (4H, d, *J* 6.9); FABMAS *m/z* 741(M⁺). Found: C, 51.74; H, 5.12; N, 3.77%. C₃₂H₃₈F₆NP requires C, 51.90; H, 5.17; N, 3.73%.

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