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Cyclo(paraquat-*o*-phenylene-paraquat-*p*-phenylene) - The Missing Isomeric Carbophane of 4,4'-Bipyridine

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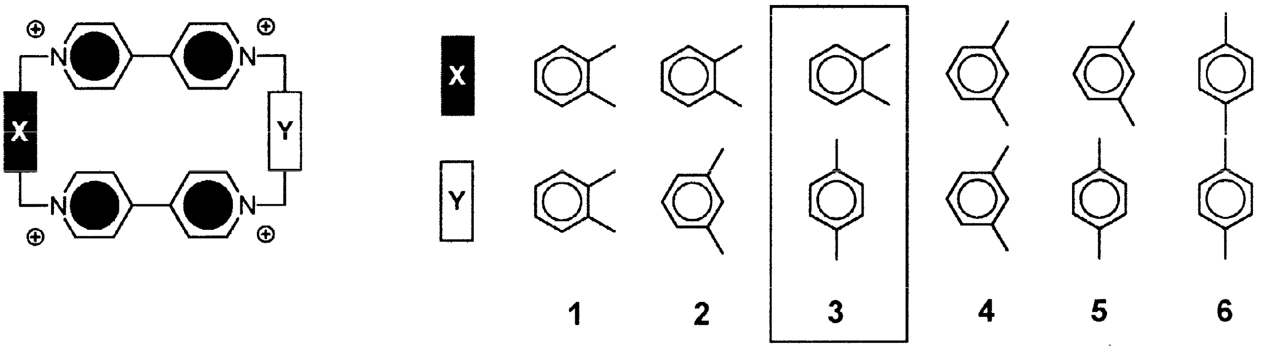
Abstract

Cyclo(paraquat-*o*-phenylene-paraquat-*p*-phenylene) **3** was synthesized by using a most simple procedure starting from an *o*-xylene bridged bis(4,4'-bipyridinium) salt. The spectroscopic and electrochemical properties of the title compound are reported.

Keywords: *4,4'-Bipyridine; Macrocycles; Cyclic Voltammetry*

Introduction

The macrocyclisation of paraquat-type salts has been reported for the first time by Hünig and coworkers [1]. The *ortho*- and *meta*-xylene bridged carbophanes **1**, **2** and **4**, respectively, were prepared by a two-step repetitive alkylation sequence in good yields. Meanwhile the crystal structure of **4**-4BF$_4$ was determined by X-ray analysis [2]. *Meta-para*-phane **5** was prepared by Vögtle and Stoddart almost at the same time [3,4]. Cyclobis(paraquat-*p*-phenylene) **6**, firstly reported by Stoddart, was proven to be an excellent receptor for the hosting of π-electron rich aromatic units [5]. Here, we report synthesis and properties of the previously unknown carbophane **3**.



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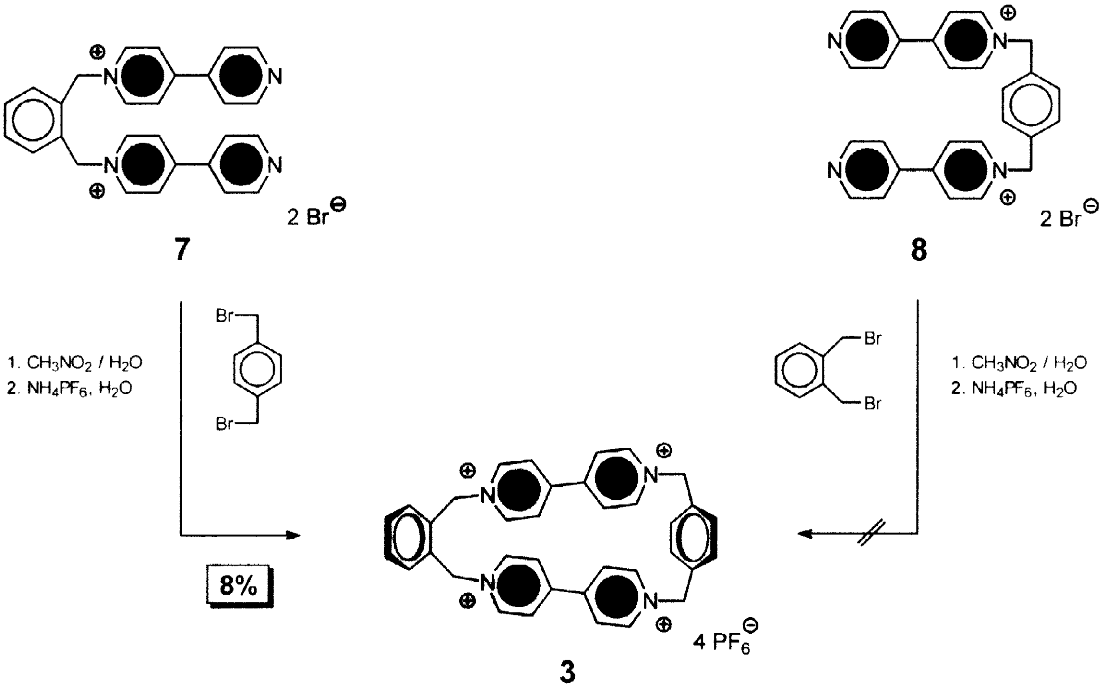
Synthesis and characterization

The *ortho*-xylene bridged dication **7** [1b] reacts with 1,4-bis(bromomethyl)benzene in a two-phase reaction at room temperature and pressure to afford after chromatographic workup and counterion exchange the desired carbophane **3** in low yield [6]. In a complementary experiment, starting from the *para*-xylene bridged bipyridinium salt **8** [1b], no formation of **3** was observed (scheme 1).

Scheme 1

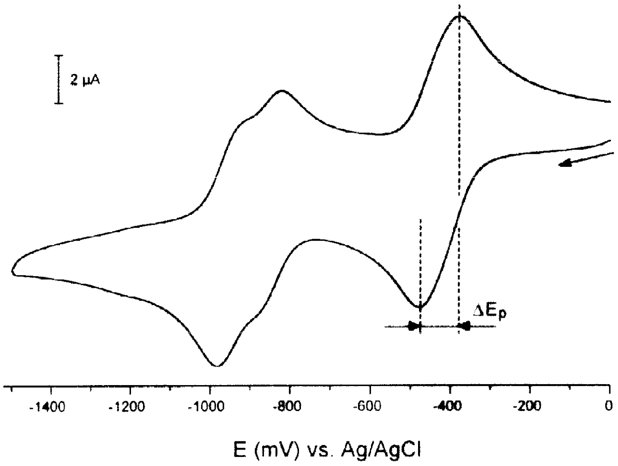


In the case of dication **8** the failed macrocyclisation can be explained by adverse geometrical suppositions. The structure of **8**-2ClO_4 was confirmed by x-ray analysis [7], and it shows that the distance between the non-alkylated nitrogen atoms amounts to 20.0 Å preferring the formation of open-chained oligomers and polymers.

The structure of macrocycle **3** was elucidated by NMR spectroscopy, mass spectroscopy and elemental analysis [6]. By use of ^1H NMR spectroscopy it could be shown, that all protons of the methylene groups are no longer equivalent and split off in AB-spin systems. For the *ortho*-xylene methylene group a coupling constant of $J = 15.0$ Hz was observed, for the *para*-xylene methylene group the value could not be determined due to signal overlap.

Electrochemistry [8]

The electrochemical reductions of the carbophanes **1**, **2** and **4-6** have previously been reported [1b,9]. Two nearly simultaneous one-electron reduction steps leading to a dicationic diradical intermediate are followed by two well separated single electron transfers providing the quinoid tetrahydrobipyridilene moiety. For **6** only two waves were observed [9d-f]. In figure 1 the cyclic voltammogram of title compound **3** is shown. The broadened first reduction wave indicates a poorly resolved separation of two redox processes. In the case of a reversible electron transfer the difference of the peak potentials (ΔE_p, belonging to a reduction-reoxidation couple) for two simultaneous electron transfer steps is in the range of 42 mV [10], while in the cyclic voltammogram of **3** a value of $\Delta E_p = 100$ mV for a scan rate of 5 mV s^{-1} has been observed, which is pointing to two overlapped one-electron transfers. Whereas the following reduction steps were successfully separated by differential pulse voltammetry, the redox potentials of the first reduction wave could not be determined by this method.



$$\log K_{comp,1} = \frac{16.9}{V}\left(E_2^0 - E_3^0\right) \quad (1)$$

$$\log K_{comp,2} = \frac{16.9}{V}\left(E_3^0 - E_4^0\right) \quad (2)$$

Figure 1. Cyclic voltammogram of 3 in DMSO at 25°C (glassy carbon electrode, 1 mM in DMSO, supporting electrolyte: 0.05 M NBu_4PF_6, scan rate 5 mV s^{-1}).

It has been shown that the difference between the redox potentials representative for the formation of the dicationic diradical (E^0_2) and the neutral molecule (E^0_4), respectively, is changing with the average distance of the bridged bipyridinium units [1]. This can be explained with the decreasing ability of an *intramolecular* comproportionation reaction in the case of a small bridge (compound **1**) up to large bridges (compounds **5**, **6**). The comproportionation constants can be calculated by equations 1 and 2 according to ref. [1b] and are given together with the observed redox potentials in table 1.

Table 1. Redox potentials and comproportionation constants of the isomeric carbophanes of 4,4'-bipyridine[a]

Compd.	$-E_1^0$	$-E_2^0$	$-E_3^0$	$-E_4^0$	$\log K_{comp,1}$	$\log K_{comp,2}$
1[b]	251		1050	1133	13.51	1.40
2[b]	306		878	1012	9.67	2.27
3	419		848	955	7.25	1.81
4[b]	429		824	907	6.68	1.40
5	427		796	872	6.24	1.28
6	283[c]		709[c]		7.20	

[a] Potentials given in mV vs. Ag/AgCl (glassy carbon electrode in DMSO at 298 K). - [b] Values for $K_{comp,1}$ and $K_{comp,2}$ were previously reported [1b]. - [c] Determined in acetonitrile vs. SSCE, values given in ref. [9d].

In good agreement with geometrical considerations carbophane **3** is arranged between the *ortho-meta* bridged and *meta-meta* bridged phanes **2** and **4**, respectively. It can be concluded that the stability of the intermediately generated dicationic diradical is comparable to that of *meta-meta*-phane **4**.

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6. Preparation and characterization of **3-4PF$_6$**: 173 mg (0.30 mmol) of **7-2Br** [1b] was dissolved in water (4 mL), 100 mg (0.38 mmol) of 1,4-bis(bromomethyl)benzene was dissolved in nitromethane (4 mL). The solutions were combined and vigorously shaken for 24 days. The aqueous phase was separated and purified by preparative TLC affording after counterion exchange with a saturated aqueous NH_4PF_6 solution pure **3-4PF$_6$** as colorless crystals. Yield 25.7 mg (8%). M.p. 235-237°C (decomp.); $R_f = 0.44$ (silica gel; MeOH/2M aq. NH_4Cl, 3:2 v/v); MS (ESI): $m/z = 955.1$ (M - PF_6); ^1H NMR (500 MHz, [D$_6$]DMSO): $\delta = 5.88$ (2 d br, 2H each, *para*-xylene-CH_2, parts of AB), 5.99 (d, $J = 15.0$ Hz, 2H, *ortho*-xylene-CH_2, part of AB), 6.34 (d, $J = 15.0$ Hz, 2H, *ortho*-xylene-CH_2, part of AB), 7.72 (s, 4H, *para*-xylene-H), 7.87, 8.01 (2 m, 2H each, *ortho*-xylene-H), 8.18, 8.28 (2 d, $J = 6.7$, 4H each, bipy-β-H), 8.83, 9.31 (2 d, $J = 6.6$, 4H each, bipy-α-H); ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): $\delta = 60.81$ (t, *ortho*-xylene-CH_2), 64.17 (t, *para*-xylene-CH_2), 126.26, 126.97 (2 d, bipy-C-β), 129.95 (d, *p*-xylene-CH), 131.61 (s, *ortho*-xylene-C-ipso), 132.24, 135.44 (2 d, *o*-xylene-CH), 138.20 (s, *para*-xylene-C-ipso), 144.70, 144.89 (2 d, bipy-C-α), 147.70, 148.42 (2 s, bipy-C-γ): $C_{36}H_{32}F_{24}N_4P_4$ (1100.5): calcd C 39.29, H 2.93, N 5.09; found C 38.90, H 3.02, N 5.07. As references for the electrochemical measurements the carbophanes **1**, **2**, **4**, and **5** were prepared and purified as described in the literature [1b, 3].
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