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Synthesis and Reactivity of a Chlorinated 1,8-Bis(diarylmethylium)naphthalenediyl Dication

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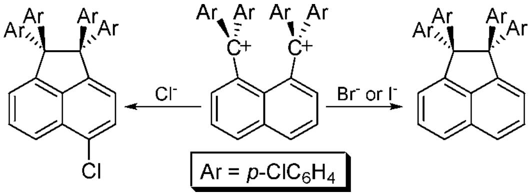
ABSTRACT



1,8-Bis(bis(*p*-chlorophenyl)methylium)naphthalenediyl dication has been prepared by treatment of the corresponding diol with a mixture of $[HBF_4]_{aq}$ and $(CF_3CO)_2O$. The proximity of the methylium centers leads to strong electrostatic repulsions that are exacerbated by the electron-withdrawing *p*-chloro substituents. As indicated by cyclic voltammetry, this dication is the strongest oxidant of the 1,8-bis(methylium)-naphthalenediyl series. It undergoes a reductive chlorination with chloride and reacts with bromide or iodide to afford the corresponding acenaphthenes.

In addition to the synthetic challenges associated with their preparation and isolation, dications[1] featuring two proximal triarylmethylium moieties linked by a 2,2′-biphenylene[2] or a [1,1′-binaphthalene]-2,2′-diyl[3] have attracted a great deal of interest because of their unusual redox properties. They undergo a two-electron reduction to afford the corresponding acenaphthenes. Because reoxidation occurs at a much more positive potential, such derivatives display redox bistability and have often been considered as switches.[2,3] In the oxidized state, these derivatives feature an intercationic separation of 3.5−3.7 Å. Speculating that a shorter intercationic separation could serve to increase the Coulombic repulsions and, therefore, electrophilic character of such compounds, we decided to investigate the use of the naphthalenediyl backbone to link two triarylmethylium moieties. As part of this effort, we have described the synthesis of two dications of general formula $[1,8\text{-}(Ar_2C)_2C_{10}H_6]^{2+}$ with Ar = *p*-MeOC$_6$H$_4$ ($\mathbf{1}^{2+}$) and C$_6$H$_5$ ($\mathbf{2}^{2+}$).[4,5] This series was complemented by Suzuki, who reported a derivative in which the diarylmethylium moieties have been replaced by the more stable methylacridium cations.[6] Structurally, these derivatives feature short intercationic separations close to 3 Å. In the absence of strongly electron-donating groups stabilizing the methylium centers, such dications display unusual reactivities. For example, $\mathbf{1}^{2+}$ reacts with hydride to afford the corresponding acenaphthene derivative.[5] A recent report by Ichikawa also indicates that $\mathbf{2}^{2+}$ is a useful organic oxidant for the self-coupling of *N*,*N*-dialkylanilines.[7] In this communication, we

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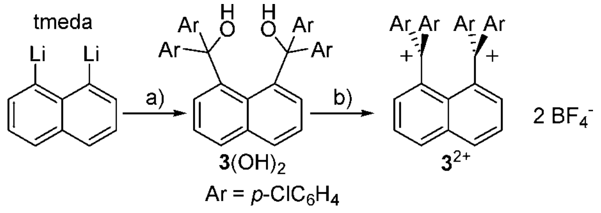
would like to report the synthesis and unusual properties of $[1,8\text{-}(p\text{-ClC}_6\text{H}_4)_2\text{C})_2\text{C}_{10}\text{H}_6]^{2+}$ ($\mathbf{3}^{2+}$) which is the most oxidizing dication thus far prepared in the 1,8-bis(methylium)-naphthalenediyl series.

The reaction of 1,8-dilithionaphthalene·TMEDA[8] with 2 molar equiv of 4,4-dichlorobenzophenone affords the corresponding diol ($\mathbf{3}$(OH)$_2$), $[1,8\text{-}(p\text{-ClC}_6\text{H}_4)_2(\text{HO})\text{C})_2\text{C}_{10}\text{H}_6]$ (Scheme 1). Upon treatment with a mixture of $[\text{HBF}_4]_{\text{aq}}$ and $(\text{CF}_3\text{CO})_2\text{O}$, this diol undergoes a double dehydroxylation reaction to afford the corresponding dication ($\mathbf{3}^{2+}$) as the BF_4^- salt (Scheme 1). The ^{1}H NMR spectrum of $\mathbf{3}^{2+}$ features the expected signals for a symmetrically *peri*-substituted naphthalene derivative with the hydrogen atoms at the 2- and 7-positions shifted downfield by 1.04 ppm with respect to the diol $\mathbf{3}$(OH)$_2$. The detection of four signals for the *p*-chlorophenyl hydrogen atoms indicates restricted motion of the aryl substituent.

Scheme 1. Synthesis of 1,8-Bis(methylium)naphthalenediyl Dication $\mathbf{3}^{2+a}$



$\mathbf{3}$(OH)$_2$

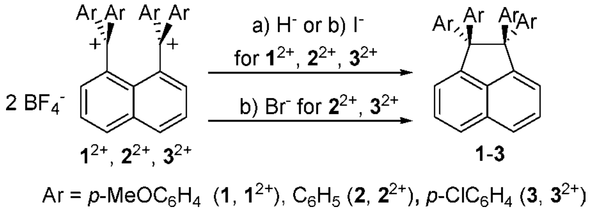
$\mathbf{3}^{2+}$

Ar = p-ClC$_6$H$_4$

[a] Reagents and conditions: (a) $(p\text{-ClC}_6\text{H}_4)_2\text{CO}$, THF, −78 °C; (b) $[\text{HBF}_4]_{\text{aq}}/(\text{CF}_3\text{CO})_2\text{O}$, 25 °C.

Unlike triarylmethylium cations, which add hydrides to afford the neutral triaryl methane derivatives,[9] treatment of $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ with LiHBEt$_3$, KH, or $(p\text{-Me}_2\text{NC}_6\text{H}_4)_3\text{CH}$ leads to reductive coupling and formation of the corresponding 1,1,2,2-tetra(aryl)acenaphthenes as observed for $\mathbf{1}^{2+}$ (Scheme 2). Since no deuterium incorporation is observed when this reaction is carried out with LiDBEt$_3$, it is reasonable to assume that this reaction proceeds through formation of a 1-diarylmethylium-8-diarylmethylnaphthalenediyl intermediate ($[\mathbf{2}\cdot\text{H}]^+$ or $[\mathbf{3}\cdot\text{H}]^+$), which then undergoes rapid deprotonation.[5] However, in light of a recent report concerning the lack of reactivity of a 1-diarylmethylium-8-diarylmethylnaphthalenediyl with hydrides,[10] an outer sphere electron-transfer reaction can also be invoked to rationalize this hydride-induced reduction. This reaction afforded isolable quantities of **2** and **3** that have been fully characterized and whose crystal structures have been determined (Figure 1).

Scheme 2. Reduction Reactions Observed of $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, and $\mathbf{3}^{2+a}$



$\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, $\mathbf{3}^{2+}$

1-3

Ar = p-MeOC$_6$H$_4$ (**1**, $\mathbf{1}^{2+}$), C$_6$H$_5$ (**2**, $\mathbf{2}^{2+}$), p-ClC$_6$H$_4$ (**3**, $\mathbf{3}^{2+}$)

[a] Reagents and conditions: (a) LiHBEt$_3$, MeCN, 25 °C; (b) for Br$^-$ and I$^-$, nBu$_4$NX (X = Br, I), MeCN, 25 °C.

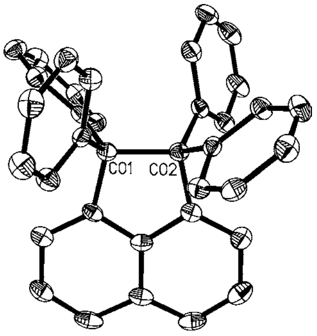


Figure 1. Ortep view of **2** showing the long C01−C02 bond of 1.701(3) Å (50% ellipsoids). H-atoms omitted for clarity.

The bonds of 1.701(3) Å (**2**) and 1.633(3) Å (**3**) linking the former methylium carbon centers are notably longer than typical C(sp^3)−C(sp^3) bonds.[6,11]

To compare the redox properties of these derivatives, the $\mathbf{2}/\mathbf{2}^{2+}$ and $\mathbf{3}/\mathbf{3}^{2+}$ redox couples were studied by cyclic voltammetry and compared to that previously reported for $\mathbf{1}/\mathbf{1}^{2+}$ (Figure 2). The cyclic voltammogram of **2** and **3** shows a two-electron oxidation peak at 1.10 V for **2** and 1.11 V for **3** (vs Fc/Fc$^+$), which corresponds to the formation of the dication $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$, respectively. This oxidation does not meet the electrochemical criteria of reversibility since

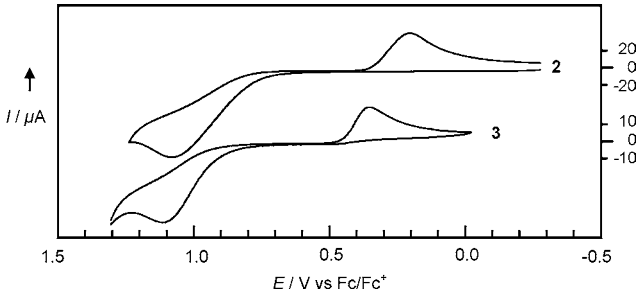


Figure 2. Cyclic voltammogram of **2** and **3** in CH$_2$Cl$_2$ with a Pt working electrode; scan rate 100 mV/sec, 0.1 M NBu$_4$PF$_6$ (vs Fc/Fc$^+$).

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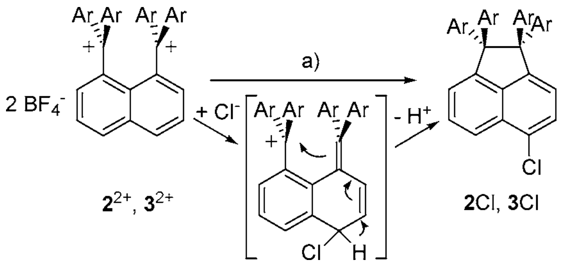
reduction of the dication occurs at a much more cathodic potential ($E_{\text{red}}(\mathbf{2}^{2+}) = 0.20$ V, $E_{\text{red}}(\mathbf{3}^{2+}) = 0.35$ V vs Fc/Fc^{+}). The reduction peak potentials measured for this series of compounds ($E_{\text{red}}(\mathbf{3}^{2+}) = 0.35 \text{ V} > E_{\text{red}}(\mathbf{2}^{2+}) = 0.20 \text{ V} > E_{\text{red}}(\mathbf{1}^{2+}) = -0.17$ V) falls in the order that can be expected on the basis of the corresponding Hammett parameters for Cl ($\sigma^{+} = 0.11$), H ($\sigma^{+} = 0$), and MeO ($\sigma^{+} = -0.78$).[12]

Following the observation that compound $\mathbf{2}^{2+}$ reacts with fluoride to afford a cation that features an unusual C−F → C bridge, we decided to investigate the reactions of $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, and $\mathbf{3}^{2+}$ with heavier halides. Although $\mathbf{1}^{2+}$ fails to react with chloride, $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ undergo a reductive chlorination reaction that affords the acenaphthenes **2**Cl and **3**Cl (Scheme 3). Both of these compounds have been fully characterized, and the crystal structure of **3**Cl has been determined. This reduction most likely proceeds by nucleophilic attack at the naphthalene 4-position followed by deprotonation at the same position. Presumably, the chloride anion is too large to enter the narrow pocket available between the methylium centers. A similar argument has been used to rationalize the anion binding selectivity of 1,8-diborylnaphthalenes, which complex fluoride but not chloride, bromide, or iodide.[13] Remarkably, treatment of $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ with bromide leads to reductive coupling and formation of the corresponding acenaphthenes **2** and **3** (Scheme 2). In the case of $\mathbf{1}^{2+}$, the reaction with bromide is very sluggish and only affords low yields of **1**. Finally, $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, and $\mathbf{3}^{2+}$ are spontaneously reduced in the presence of iodide (Scheme 2). The coupling reactions observed in the presence of bromide anion are especially surprising and substantiate the unusual oxidant properties of $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$.

Scheme 3. Reductive Chlorination Reactions Observed for $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ in the Presence of Chloride[a]



[a] Reagents and conditions: (a) KCl/18-crown-6, MeCN, 25 °C.

The reactivity of $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, and $\mathbf{3}^{2+}$ results from the unique structural and electronic properties of the dications. The proximity of the methylium centers leads to increased electrostatic repulsive interactions and favors any reactions that will allow for their removal. These effects are further exacerbated by the presence of the electron-withdrawing *p*-chloro substituents in $\mathbf{3}^{2+}$, which on the basis of its electrochemistry is the strongest oxidant of the series. Attempts to introduce more electron-withdrawing substituents at the *para*-position of the phenyl rings have thus far been unsuccessful.

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Supporting Information Available: Experimental procedures, analytical data, and X-ray structure data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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