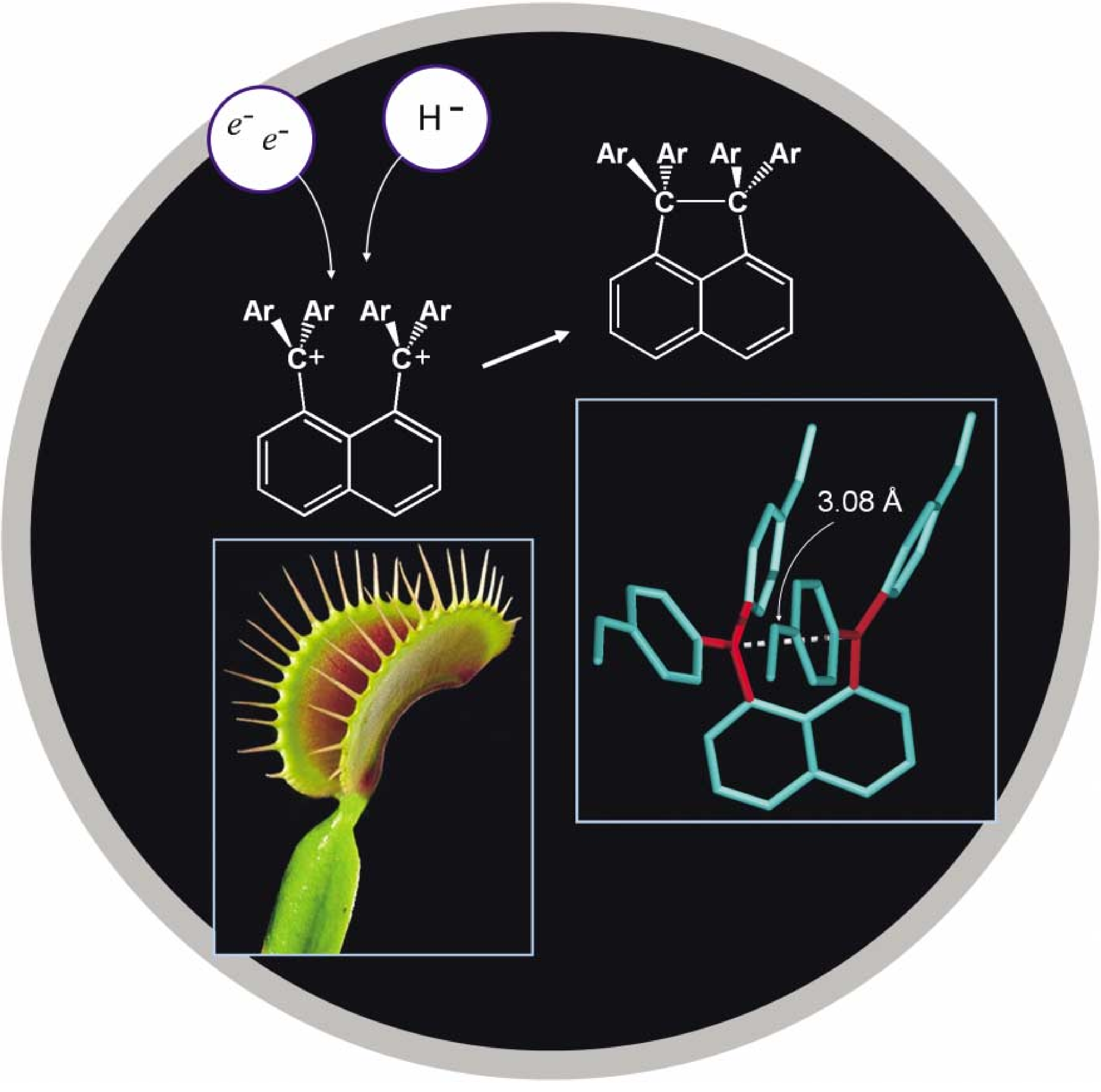
Zuschriften



Die erzwungene Nähe der Methylium-Zentren im 1,8-Bis(bis(*p*-methoxyphenyl)methylium)naphthalindiyl-Dikation verstärkt seine Elektronenaffinität. Ähnlich wie die Venusfliegenfalle Insekten verschlingt, fängt dieses Dikation Elektronen und hält sie in einer neu gebildeten C-C-Bindung fest. Mehr dazu entnehmen Sie der folgenden Zuschrift von F. P. Gabbaï und H. Wang.

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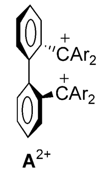
Arene Electrochemistry

Synthesis and Reactivity of a 1,8-Bis(methylium)naphthalenediyl Dication**

*Huadong Wang and François P. Gabbaï**

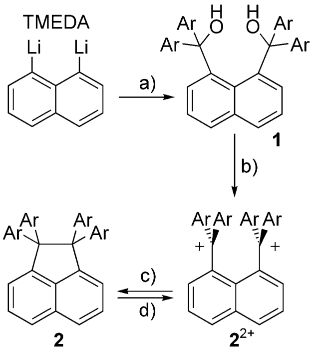
Triarylmethylium cations constitute one of the best studied classes of stable carbocations.[1,2] In addition to being used as dyes,[3] such species have become ubiquitous in the domain of olefin polymerization catalysis where they serve as activators.[4] Recent advances in the chemistry of these compounds focus on their incorporation in bifunctional derivatives. Among these,[5] a series of dicationic systems in which two triarylmethylium cations are linked by a biphenyl (as in **A**$^{2+}$) or a binaphthyl backbone have been prepared and have been shown to display unique electrochromic properties.[6,7] Structural studies indicate that the methylium centers of these biphenyl- or binaphthyl-based systems are separated by only 3.5–3.7 Å. Owing to inherent coulombic repulsions, it can be assumed that the physical separation between the methylium centers governs the stability and reactivity of such derivatives. Hence, control over this separation could serve to fine-tune the electrophilic and Lewis acidic properties of such bifunctional molecules. Applying this paradigm to the synthesis of highly electrophilic and Lewis acidic bidentate molecules, we are now targeting bis(methylium) dications that feature short intercationic separation. Herein, we report on the synthesis, characterization, and reactivity of 1,8-bis(bis(*p*-methoxyphenyl)methylium) naphthalenediyl dication (**2**$^{2+}$), which features two methylium centers separated by 3.076(2) Å.



A^{2+}

Ar = *p*-MeOC$_6$H$_4$

The reaction of 1,8-dilithionaphthalene·TMEDA[8] with two molar equivalents of 4,4-dimethoxybenzophenone affords the corresponding diol, namely 1,8-bis[bis(*p*-methoxyphenyl)hydroxymethyl]naphthalene (**1**) (Scheme 1). Upon treatment with a mixture of aq [HBF$_4$] and (CF$_3$CO)$_2$O, this diol undergoes a double dehydroxylation reaction to afford the corresponding dication, **2**$^{2+}$ (Scheme 1). The ^{1}H NMR spectrum of **2**$^{2+}$ features the expected signals for a symmetrically *peri*-substituted naphthalene derivative: the signals for the hydrogen atoms at the 2- and 7-positions are shifted downfield by 1.05 ppm with respect to the analogous signals of **1**. The appearance of four distinct signals for the hydrogen attached to the aromatic core of the *p*-methoxyphenyl groups indicates restricted rotation of the latter. The ^{13}C resonance of the carbocationic centers appears at $\delta = 191.8$ ppm, which is comparable to that observed for other carbocations such as bis(4-methoxyphenyl)phenylmethylium.[9]



Scheme 1. Synthesis of **2**$^{2+}$ and **2**. Ar = *p*-MeO(C$_6$H$_4$). a) Ar$_2$CO in THF at −78 °C; b) aq [HBF$_4$]/(CF$_3$CO)$_2$O; c) Li[BEt$_3$H] in THF; d) aq [HBF$_4$]/CF$_3$CO$_2$H. TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

A single-crystal X-ray analysis[10] revealed the existence of a sterically congested structure (Figure 1, top). The tight geometrical constraints present in the structure of **2**$^{2+}$ induce distortions of the naphthalenediyl skeleton. Especially noteworthy are the C9-C8-C02 and C9-C1-C01 angles (125.36(16) and 126.60(15)°, respectively) which are larger than the ideal value of 120°. As indicated by the sum of the bond angles at C01 ($\Sigma_{(\text{C-C}_{01}\text{-C})} = 359.6$) and C02 ($\Sigma_{(\text{C-C}_{02}\text{-C})} = 359.8$), each methylium center adopts a trigonal-planar arrangement. The trigonal coordination planes of the C01 and C02 centers form relatively large dihedral angles with the plane containing the naphthalene backbone (59.7 and 59.6°, respectively), indicating that conjugation of the methylium center empty p_z orbital with the π-system of the naphthalene backbone can only be modest. By contrast, the *p*-methoxyphenyl groups strongly stabilize the methylium centers, as indicated by the small dihedral angles that they form with the trigonal coordination planes of the C01 and C02 centers (18.1–28.5°). This mesomeric stabilization is also reflected by the short C01−C11, C01−C21, C02−C31, and C02−C41 bonds. Finally, as a result of this unique molecular structure, the vicinal methylium centers are separated by 3.076(2) Å, which is the shortest such distance so far reported.[5–7]

The structure of **2**$^{2+}$ was computationally optimized using DFT methods (B3LYP, 6-31 + G* for the methylium carbon centers, 6-31G for all other atoms).[11] The fully optimized geometry approaches that observed for the dication in [**2**$^{2+}$][BF$_4^-$]$_2$. Most importantly, examination of the DFT orbitals reveals that the methylium p_z orbitals largely contribute to the LUMO and are oriented toward one another in a trans-annular fashion (Figure 1, bottom). Thus, **2**$^{2+}$ is both structurally and electronically similar to 1,8-bis(diphenylboryl)naphthalene, which features an interboron separation of 3.002(2) Å and whose LUMO bears strong contributions from the converging 2p_z boron orbitals.[12]

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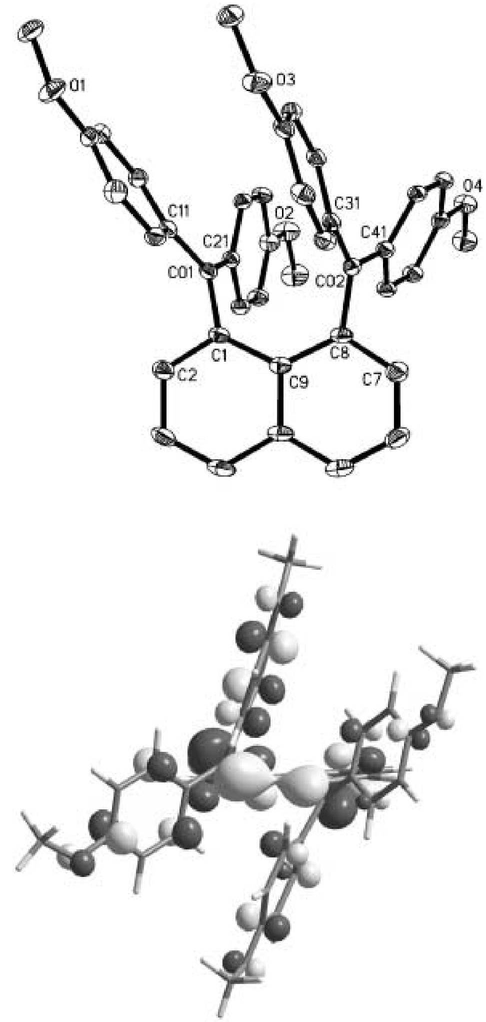


Figure 1. Top: ORTEP plot of the molecular structure of $\mathbf{2}^{2+}$ in $[\mathbf{2}^{2+}][BF_4^-]_2(MeCN)_2$ with thermal ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: C01-C02 3.076(2), C01-C11 1.418(2), C01-C21 1.440(2), C01 C1 1.483(2), C02-C41 1.430(2), C02-C31 1.432(2), C02-C8 1.482(2); C11-C01-C21 124.06(16), C11-C01-C1 117.59(15), C21-C01-C1 118.00(15), C41-C02-C31 123.65(15), C41-C02-C8 117.48(15), C31-C02-C8 118.64(15), C2-C1-C01 113.78(16), C9-C1-C01 126.60(15), C7-C8-C02 114.71(16), C9-C8-C02 125.36(16). Bottom: DFT orbital picture showing the LUMO in $\mathbf{2}^{2+}$.

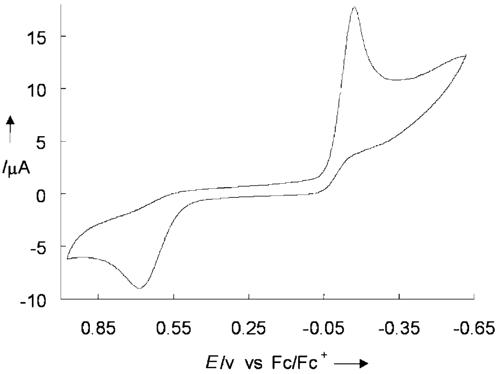
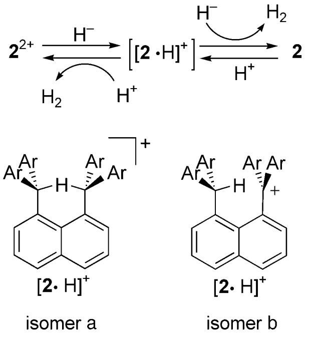


Figure 2. Cyclic voltammogram of $\mathbf{2}^{2+}$ in CH_2Cl_2 with a Pt working electrode; scan rate: 100 $mV\,s^{-1}$, 0.1 M NBu_4PF_6.

The cyclic voltammogram of $\mathbf{2}^{2+}$ shows a two-electron reduction wave at −0.17 V (vs Fc/Fc$^+$), corresponding to the formation of acenaphthylene **2** (Figure 2). As a confirmation, the same voltammogram is obtained when starting from pure **2** (vide infra). The reduction of $\mathbf{2}^{2+}$ does not meet the electrochemical criteria of reversibility, and reoxidation necessitates a more positive potential of 0.68 V (vs Fc/Fc$^+$). In comparison to 2,2′-bis(bis(*p*-methoxyphenyl)methylium)-biphenyl ($\mathbf{A}^{2+}$), whose reduction occurs at −0.28 V,[6a,13] reduction of $\mathbf{2}^{2+}$ appears remarkably facile as it is shifted by more than 0.11 V toward cathodic potentials. In turn, this difference provides a measure of the cooperative effects that result from the proximity of the neighboring methylium centers in $\mathbf{2}^{2+}$; it also reflects the increased electrophilicity of $\mathbf{2}^{2+}$. We also note that the oxidation of **2** into $\mathbf{2}^{2+}$ necessitates a less cathodic potential (0.68 V) than that observed for its biphenyl analogue (oxidation at 1.01 V).

It is well known that triarylmethylium cations add hydrides to afford the neutral triaryl methane derivatives.[14] In the present case, however, treatment of $\mathbf{2}^{2+}$ with $LiHBEt_3$, KH, or $(p\text{-}Me_2NC_6H_4)_3CH$ leads to reductive coupling and formation of **2**, which is accompanied by gas evolution (Scheme 1). Reaction with $LiDBEt_3$ does not lead to any deuterium incorporation, ruling out a mechanism in which the hydride would attack one of the aromatic rings. Hence, we propose that this reaction proceeds through formation of $[\mathbf{2}{\cdot}H]^+$, which undergoes rapid deprotonation (Scheme 2). By analogy with the reactivity of 1,8-diborylnaphathlene hydride sponges,[15] it is tempting to suggest that intermediate $[\mathbf{2}{\cdot}H]^+$ possesses a C–H–C 3c–2e bridge ($[\mathbf{2}{\cdot}H]^+$ isomer a).[16] However, we have not been able to confirm this formulation, and an unsymmetrical structure should also be considered ($[\mathbf{2}{\cdot}H]^+$ isomer b) (Scheme 2). In the presence of a substoichiometric amount of $LiHBEt_3$, only mixtures of **2** and $\mathbf{2}^{2+}$ are observed. This suggests that the proposed intermediate $[\mathbf{2}{\cdot}H]^+$ is labile and can revert to the dication $\mathbf{2}^{2+}$ by extrusion of a hydride.



Scheme 2. Proposed pathways for the reactions of $\mathbf{2}^{2+}$ with hydrides and of **2** with protons.

We have determined the crystal structure of **2**.[10] Remarkably, the bond of 1.670(3) Å linking the former methylium carbon centers constitutes one of the longest $C(sp^3)-C(sp^3)$ bonds so far reported.[17,18] Because of this lengthening, this bond can be anticipated to be inherently weak and therefore possibly reactive. As a matter of fact, **2** undergoes a slow oxidation reaction when treated with aq $[HBF_4]/CF_3CO_2H$ leading to the formation of $\mathbf{2}^{2+}$, which could be isolated in 55–70 % yield (Scheme 2). While Brønsted acids are known to act as oxidants in the formation of carbenium ions,[19] formation of two methylium centers by oxidative protonolysis of a $C(sp^3)-(sp^3)$ bond remains unprecedented.[20] Moreover, we note that acid-induced C–C bond activations typically necessitate the use of superacidic media.[21] This oxidation reaction likely proceeds by protonation of **2**, which under acidic conditions extrudes a hydride to afford $\mathbf{2}^{2+}$. Once again, the intermediacy of $[\mathbf{2}{\cdot}H]^+$ can be invoked (Scheme 2). Theoretical investigations are currently underway to support this proposal.

In summary, we report the first stable compound featuring two methylium cation centers directly connected by a *peri*-substituted naphthalene backbone. The enforced proximity of the methylium centers in $\mathbf{2}^{2+}$ intensifies the electron affinity of this unusual molecule. In the presence of hydrides, this dication undergoes reductive coupling which also leads to the formation of **2**. The newly formed C–C bond of the latter is long and undergoes an oxidative protonolysis reaction which affords $\mathbf{2}^{2+}$.

Experimental Section

1: A solution of 4,4-dimethoxylbenzophenone (1.12 g, 4.52 mmol) in THF (15 mL) was added to a solution of 1,8-dilithionaphthalene (0.50 g, 1.95 mmol) in THF (5 mL) at −78 °C. The reaction mixture was stirred for 2 h at −78 °C and for another 12 h at room temperature. After addition of 5 % aq NH_4Cl (20 mL) the organic phase was extracted with ether, dried with $MgSO_4$, and concentrated. Column chromatography on silica gel (*n*-hexane/ethyl acetate 6:1) afforded **1** (0.51 g, 43 %) as a light yellow solid. ^1H NMR ($CDCl_3$, 500 MHz): $\delta =$ 3.73 (s, 12 H, CH_3), 6.55 (d, $J = 8.8$ Hz, 8 H, C_6H_4), 6.92 (d, $J = 7.3$ Hz, 2 H, H_{Naph}), 6.97 (d, $J = 8.8$ Hz, 8 H, C_6H_4), 7.37 (t, $J = 7.8$ Hz, 2 H, H_{Naph}), 7.80 ppm (d, $J = 8.3$ Hz, 2 H, H_{Naph}); ^{13}C NMR ($CDCl_3$, 125.9 MHz) $\delta = 55.3$, 85.1, 112.7, 113.2, 123.2, 129.0, 129.2, 131.0, 133.5, 141.9, 142.8, 158.4 ppm; Elemental analysis calcd (%) for $C_{40}H_{36}O_6{\cdot}0.85\,CHCl_3$: C 68.70, H 5.20; found: C 68.82, H 5.10.

$[\mathbf{2}^{2+}][BF_4^-]_2$: A suspension of **1** (0.19 g, 0.31 mmol) in $(CF_3CO_2)O$ (5 mL) was treated with aq $[HBF_4]$ (48 %, 0.20 mL, 1.5 mmol). The reaction mixture was stirred for 2 h before Et_2O (20 mL) was added to the mixture, which resulted in precipitation of the product as a dark-red solid. It was washed with small portions of Et_2O to afford a $[\mathbf{2}^{2+}][BF_4^-]_2$ (0.19 g, yield 79 %). Single crystals of $[\mathbf{2}^{2+}][BF_4^-]_2{\cdot}(MeCN)_2$ were obtained by vapor diffusion of diethyl ether into a solution of $[\mathbf{2}^{2+}][BF_4^-]_2$ in acetonitrile. ^1H NMR ($[D_6]$acetone, 500 MHz): $\delta =$ 4.19 (s, 12 H, CH_3), 6.97 (dd, $J = 2.2$, 9.0 Hz, 4 H, C_6H_4), 7.17 (dd, $J = 9.0$, 2.7 Hz, 4 H, C_6H_4), 7.27 (d, $J = 8.6$ Hz, 4 H, C_6H_4), 7.67 (dd, $J =$ 1.2, 7.3 Hz, 2 H, H_{Naph}), 7.89 (dd, $J = 2.4$, 9.2 Hz, 4 H, C_6H_4), 8.03 (dt, $J = 0.9$, 7.8 Hz, 2 H, H_{Naph}), 8.85 ppm (dd, $J = 1.2$, 8.3 Hz, 2 H, H_{Naph}); ^{13}CNMR ($[D_6]$acetone, 125.9 MHz): $\delta = 57.7$, 117.8, 118.1, 127.3, 131.4, 135.2, 135.7, 136.9, 138.7, 142.8, 144.2, 145.6, 172.9, 191.8 ppm; Elemental analysis calcd (%) for $C_{40}H_{34}O_4B_2F_8{\cdot}2\,CH_3CN$: C 62.25, H 4.98; found: C 61.71, H 4.75. UV/Vis (CH_3CN): $\lambda_{max}(\log(\varepsilon)) = 482$ (5.46).

2: A solution of $LiBEt_3H$ in THF (1.0 M, 0.5 mL, 0.5 mmol) was added to a stirred solution of $[\mathbf{2}^{2+}][BF_4^-]_2$ (53 mg, 70 µmol) in THF (10 mL) at room temperature. After 30 min the reaction mixture was quenched by adding 5 % aq NH_4Cl (20 mL). The organic phase was extracted with ether, dried with $MgSO_4$, and concentrated. Column chromatography on silica gel (*n*-hexane/ethyl acetate 8:1) afforded **2** (30 mg, 74 %) as a light yellow solid. Single crystals of **2** suitable for X-ray structural analysis were obtained by slow evaporation of the solvent from a solution of **2** in acetonitrile. ^1H NMR ($[D_6]$acetone, 500 MHz): $\delta = 3.67$ (s, 12 H, CH_3), 6.50 (d, $J = 8.5$ Hz, 8 H, C_6H_4), 6.84 (d, $J = 8.8$ Hz, 8 H, C_6H_4), 7.23 (d, $J = 7.1$ Hz, 2 H, H_{Naph}), 7.60 (t, $J =$ 7.3 Hz, 2 H, H_{Naph}), 7.82 ppm (d, $J = 8.3$ Hz, 2 H, H_{Naph}); ^{13}C NMR ($[D_6]$acetone, 125.9 MHz): $\delta = 54.6$, 73.4, 112.0, 112.5, 123.4, 128.3, 131.8, 136.9, 137.8, 150.8, 157.6 ppm; Elemental analysis calcd (%) for $C_{40}H_{34}O_4$: C 83.02, H 5.92; found: C 82.59, H 5.90.

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Keywords: arenes · carbocations · cooperative effects · electrochemistry · Lewis acids

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[10] Crystal data: $[\mathbf{2}^{2+}][BF_4^-]_2{\cdot}(MeCN)_2$: $C_{44}H_{40}O_4B_2F_8N_2$, $M_r =$ 834.40, monoclinic, space group $P2(1)/n$, $a = 7.7412(17)$, $b =$ 30.885(7), $c = 16.494(4)$ Å, $\beta = 94.675(4)°$, $V = 3930.5(15)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.410\ g\,cm^{-3}$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T =$ 110(2) K, 29394 measured reflections, 9351 unique, $R_{int} = 0.0729$, $R_1 = 0.0560$, $wR_2 = 0.1397$ (all data). **2**: $C_{40}H_{34}O_4$, $M = 578.71$, triclinic, space group $P\bar{1}$, $a = 10.0914(17)$, $b = 10.8633(19)$, $c =$ 15.308(3) Å, $\alpha = 101.893(3)°$, $\beta = 98.924(3)°$, $\gamma = 111.528(3)°$, $V = 1477.7(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.301\ g\,cm^{-3}$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 110(2)$ K, 12635 measured reflections, 6539 unique, $R_{int} = 0.0424$, $R_1 = 0.0633$, $wR_2 = 0.1306$ (all data). The crystals (0.23 × 0.22 × 0.11 mm for $[\mathbf{2}^{2+}][BF_4^-]_2{\cdot}(MeCN)_2$ and 0.46 × 0.27 × 0.11 mm for **2**) were mounted onto a glass fiber with Apiezon grease. All the structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms. CCDC-220813 and 220814 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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