Tris(1-naphthyl)- and tris(2-naphthyl)methyl cations: highly crowded triarylmethyl cations[1]

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The highly hindered tris(1-naphthyl)methyl and tris(2-naphthyl)methyl cations **3** and **5** have been prepared under long lived stable ion conditions and characterized by ^{13}C NMR spectroscopy at low temperatures. The latter can abstract hydride from cycloheptatriene to afford tris(2-naphthyl)methane **7**, but the reaction of cycloheptatriene with the more crowded cation **3** failed to give the corresponding hydrocarbon. A primary kinetic isotope effect, $k_H/k_D = 7.1 \pm 0.5$, found in the former case supports a colinear hydride abstraction mechanism. The ions **3** and **5** upon quenching rearranged to give a mixture of isomeric 13-(1-naphthyl)-1,2,7,8-dibenzofluorene **4** and 13-(2-naphthyl)-2,3,6,7-dibenzofluorene **6**, respectively.

Introduction

Stable triarylmethyl cations have been widely studied. Previously known triarylmethyl cations are quite stable, even at room temperature.[2] The structures of several such cations have been established by X-ray crystallography and by NMR studies.[3,4] The only example, however, of a sterically overcrowded triarylmethyl cation known to us is tris(1-azulenyl)-methyl cation,[5] which is stable enough to be isolated at room temperature.

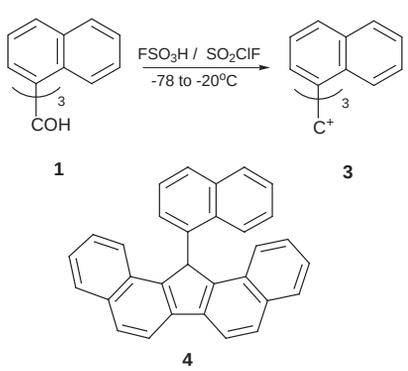
With our interest in the chemistry and structure of carbocations, we have sought to investigate crowded triarylmethyl carbocations that may exhibit unusual stability or reactivity. So far the most highly crowded trialkylmethyl cation reported, the tris(1-adamantanyl)methyl cation, was prepared under stable ion conditions in our laboratory.[6] Despite extensive studies on triarylmethyl cations, no investigation of tris(naphthyl)methyl cations has yet been reported. It was of interest to us to establish the stability of tris(naphthyl)methyl cations in relation to triphenylmethyl cation and determine whether overcrowding would significantly diminish aromatic delocalization through rotation of the aryl π-system out of the carbocationic plane. In continuation of our studies, we wish to report here the preparation of tris(1-naphthyl)methyl and tris(2-naphthyl)methyl cations and two very crowded triarylmethyl cations. The low temperature ^{13}C NMR studies on both of them, their reactivity, and their tendency for rearrangement proved to be unusual and interesting.

Results and discussion

The preparation of tris(1-naphthyl)methyl and tris(2-naphthyl)methyl cations was undertaken by the ionization of the corresponding alcohols, tris(1-naphthyl)- and tris(2-naphthyl)-methanols **1** and **2**. Alcohols **1** and **2** were obtained by the reaction of 1-naphthoyl chloride and 1-naphthyllithium and the reaction of 2-naphthoyl chloride and 2-naphthyllithium, respectively.

Initially the usual methods used for obtaining triphenylmethyl cation[7] were attempted to prepare the tris(1-naphthyl)-methyl cation from the alcohol **1**. When **1** was treated with HBF_4 or $HClO_4$ in acetic anhydride at 20 °C, the reaction did not give the desired salt of **3**, tris(1-naphthyl)methyl fluoroborate or perchlorate. Instead 13-(1-naphthyl)-1,2,7,8-dibenzofluorene **4** was obtained in quantitative yield.

Successful preparation of tris(1-naphthyl)methyl cation **3** was subsequently achieved under stronger superacidic conditions by the reaction of tris(1-naphthyl)methanol **1** with FSO_3H–SO_2ClF at low temperature (−78 to −20 °C). When **1** was treated with a mixture of FSO_3H and SO_2ClF at −78 °C, a dark blue solution resulted.



Scheme 1

The ^{13}C NMR spectrum at −40 °C showed that ion **3** had been formed. The chemical shift of the characteristic carbocationic center was δ ^{13}C 198.6, shielded from C^+ of the triphenylmethyl cation by 14 ppm. This indicates enhanced charge dispersal into the electron-rich naphthalene rings. In addition to the cationic carbon resonance, a total of 29 ^{13}C NMR peaks (see experimental section for multiplicity assignment) were observed between δ ^{13}C 124.2 and 146.6. These data clearly indicate that carbocation **3** exists as two conformational isomers with overlapping carbocationic centers (at least at 50 MHz ^{13}C spectrometer frequency). We suggest that these isomers are the symmetrical and unsymmetrical helical conformational isomers. The MMX[8] calculated energy barrier between them is substantial, and they would not be expected to interconvert at a measurable rate, even at room temperature.

Carbocation **3** is considerably less stable than the triphenyl-

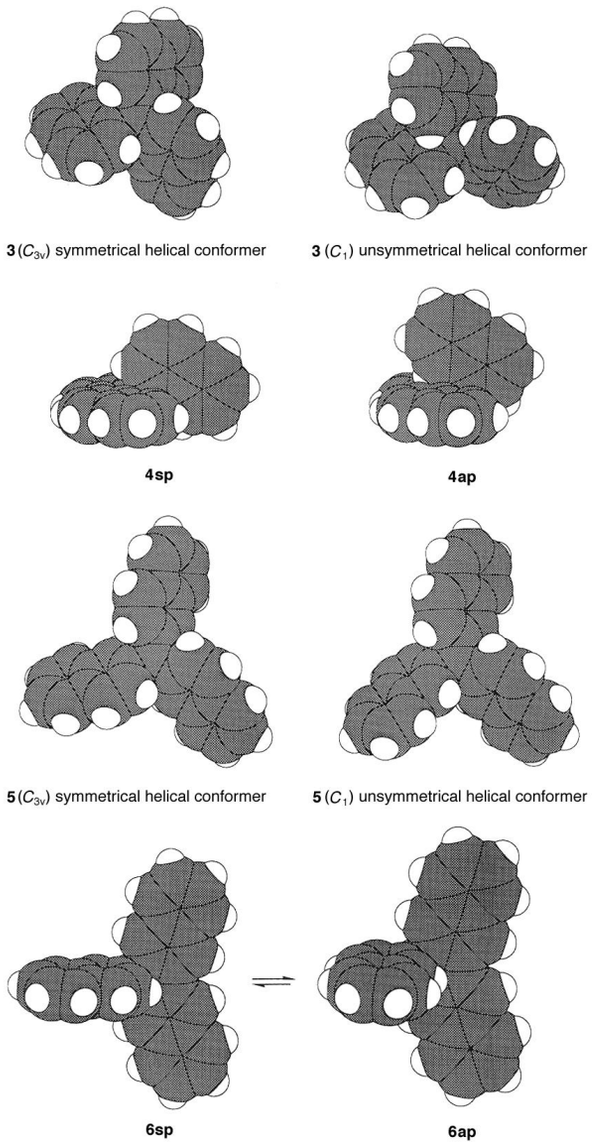


Fig. 1 Space-filling structures of **3**–**6** computed using MMX in PC Model 4.3 and drawn using Chem 3D plus 2.0.1.

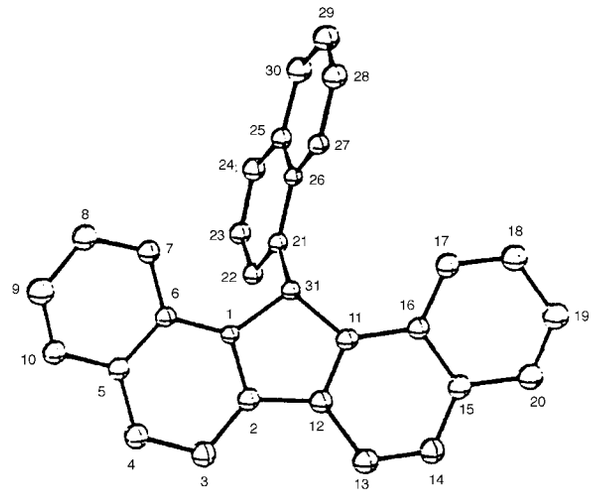


Fig. 2 X-Ray structure of **4sp**. Hydrogen atoms are omitted for clarity. Bond distances (Å) and bond angles (°): C^1–C^2, 1.383 (17), C^2–C^3, 1.406 (16), C^3–C^4, 1.431 (17), C^4–C^5, 1.438 (18), C^5–C^6, 1.444 (15), C^6–C^7, 1.404 (17), C^7–C^8, 1.437 (16), C^8–C^9, 1.400 (20), C^9–C^{10}, 1.381 (22), C^{10}–C^5, 1.406 (18), C^{11}–C^{12}, 1.379 (17), C^{12}–C^{13}, 1.439 (17), C^{13}–C^{14}, 1.362 (18), C^{14}–C^{15}, 1.436 (21), C^{15}–C^{16}, 1.452 (18), C^{16}–C^{17}, 1.435 (18), C^{17}–C^{18}, 1.413 (16), C^{18}–C^{19}, 1.477 (21), C^{19}–C^{20}, 1.382 (23), C^{20}–C^{15}, 1.444 (16), C^{21}–C^{22}, 1.390 (16), C^{22}–C^{23}, 1.406 (16), C^{23}–C^{24}, 1.358 (18), C^{24}–C^{25}, 1.415 (18), C^{25}–C^{26}, 1.457 (14), C^{26}–C^{27}, 1.422 (15), C^{27}–C^{28}, 1.386 (16), C^{28}–C^{29}, 1.447 (18), C^{29}–C^{30}, 1.386 (16), C^{30}–C^{25}, 1.422 (15), C^1–C^{31}, 1.546 (14), C^{11}–C^{31}, 1.507 (15), C^1–C^2–C^3, 123.3 (1.2), C^2–C^3–C^4, 117.1 (1.2), C^3–C^4–C^5, 120.3 (1.2), C^4–C^5–C^6, 120.1 (1.2), C^5–C^6–C^7, 120.8 (1.2), C^6–C^7–C^8, 118.6 (1.2), C^7–C^8–C^9, 118.9 (1.4), C^8–C^9–C^{10}, 123.2 (1.4), C^9–C^{10}–C^5, 119.2 (1.4), C^{10}–C^5–C^6, 119.3 (1.3), C^{10}–C^5–C^4, 120.4 (1.2), C^1–C^6–C^7, 121.3 (1.1), C^{11}–C^{12}–C^{13}, 124.7 (1.1), C^{11}–C^{12}–C^2, 108.5 (1.0), C^{12}–C^{13}–C^{14}, 115.6 (1.3), C^{13}–C^{14}–C^{15}, 123.1 (1.2), C^{14}–C^{15}–C^{16}, 119.9 (1.2), C^{14}–C^{15}–C^{20}, 120.4 (1.4), C^{20}–C^{15}–C^{16}, 119.7 (1.5), C^{15}–C^{16}–C^{11}, 116.9 (1.3), C^{15}–C^{16}–C^{17}, 119.5 (1.1), C^{11}–C^{16}–C^{17}, 123.5 (1.2), C^{16}–C^{17}–C^{18}, 121.0 (1.3), C^{17}–C^{18}–C^{19}, 118.0 (1.5), C^{18}–C^{19}–C^{20}, 122.1 (1.4), C^{19}–C^{20}–C^{15}, 119.6 (1.5), C^6–C^1–C^{31}, 128.0 (1.0), C^2–C^1–C^{31}, 110.7 (0.9), C^1–C^2–C^{12}, 107.7 (1.1), C^3–C^2–C^{12}, 128.6 (1.2), C^{31}–C^{21}–C^{22}, 117.9 (1.1), C^{26}–C^{21}–C^{22}, 120.9 (1.0), C^{21}–C^{22}–C^{23}, 120.7 (1.2), C^{22}–C^{23}–C^{24}, 121.4 (1.2), C^{23}–C^{24}–C^{25}, 119.0 (1.1), C^{24}–C^{25}–C^{26}, 121.3 (1.2), C^{26}–C^{25}–C^{30}, 117.6 (1.2), C^{25}–C^{26}–C^{21}, 116.6 (1.1), C^{25}–C^{26}–C^{27}, 118.7 (1.1), C^{26}–C^{27}–C^{28}, 121.9 (1.2), C^{27}–C^{28}–C^{29}, 121.0 (1.3), C^{28}–C^{29}–C^{30}, 117.4 (1.3), C^{29}–C^{30}–C^{25}, 123.3 (1.2), C^1–C^{31}–C^{11}, 100.9 (0.8), C^{11}–C^{31}–C^{21}, 113.7 (0.9), C^1–C^{31}–C^{21}, 108.9 (0.8).

methyl cation; when the solution of **3** was quenched with ice–water, it gave 13-(1-naphthyl)-1,2,7,8-dibenzofluorene **4** through 1,5-cyclization. Such cyclization in triphenylmethyl cation to yield 9-phenylfluorene has been previously recognized.[9] Quenching of the cation **3** at −78 °C also resulted in **4** (56% yield) along with the starting alcohol **1**. To rule out any contamination of isomeric protonated 13-(1-naphthyl)-1,2,7,8-dibenzofluorene **4** in the ionization of **1**, we independently protonated **4** in FSO_3H–SO_2ClF at −78 °C. Under these conditions no discernible peaks were observed in the ^{13}C NMR spectrum indicating extensive decomposition. Thus we believe that 1,5-cyclization of **3** to give **4** takes place only during quenching. Attempted hydride abstraction of cycloheptatriene with **3** to give tropylium ion was unsuccessful as no reaction was observed (*vide infra*).

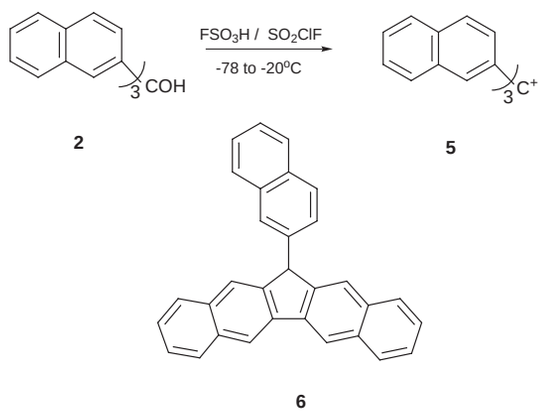
Two conformational isomers, **4ap** and **4sp** of 13-(1-naphthyl)-1,2,7,8-dibenzofluorene **4** (Fig. 1), were observed in the ^1H NMR spectrum of the mixture at room temperature. The MMX calculated energy barrier between them is extremely high and thus they cannot interconvert at room temperature.

The ratio of **4sp** to **4ap** is about 3 : 1. Isomer **4sp** was successfully isolated as single crystals by recrystallization of the mixture of **4** from acetone. The structure of **4sp** was confirmed by single crystal X-ray crystallographic analysis and is shown in Fig. 2.

The striking contrast of intrinsic stability between the triphenylmethyl cation and cation **3** suggests significant steric deformation in the latter from the carbocationic plane. We calculated the preferred geometry of the conformers using the molecular mechanics program.[8] Two conformers were indicated as the most stable forms of cation **3**, a symmetrical helical conformer (C_{3v} symmetry) and an unsymmetrical helical conformer (C_1 symmetry). Examination of the bond rotation necessary to interconvert these conformers using a rigid sphere approximation with the molecular mechanics calculation leads to the conclusion that the conformers cannot interconvert at or near room temperature (E_a in excess of 100 kcal mol^{-1}). Hence this pair of cations [**3**(C_{3v}) and **3**(C_1)] constitute a pair of conformational isomers. Molecular mechanics calculations for the helical conformations led us to estimate a p–pπ interorbital angle of 50° between the contiguous cationic and the aromatic p orbitals, suggesting poor overlap and thus explaining the decreased stability with respect to the triphenylmethyl cation. Interconversion of the α- and β-helical conformers requires cooperative rotation and may itself be a highly unfavorable process, probably inaccessible at room temperature. Regarding the formation of **4** upon quenching ion **3**, it is reasonable to suggest that **2**(C_{3v}) and **2**(C_1) are converted stereoselectively to **4sp** and **4ap**, respectively. A mechanism involving Friedel–Crafts cycloalkylation and 1,3-sigmatropic rearrangement would rationalize the transformation. Attempts to quench **3** with hydride donors such as cycloheptatriene or triethyl-

silane to obtain the parent tris(1-naphthyl)methane were not successful.

Tris(2-naphthyl)methyl cation **5** was also successfully prepared by the ionization of tris(2-naphthyl)methanol **2** in



2 **5**

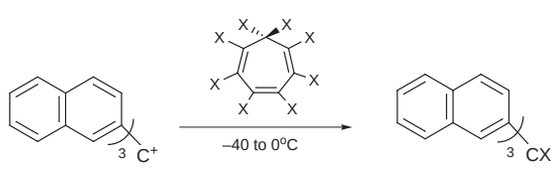
6

Scheme 2

FSO_3H– SO_2ClF at −78 °C. However, attempts to isolate either the perchlorate or tetrafluoroborate salt of **5** at room temperature were unsuccessful. Cation **5** shows the carbocationic center peak at δ ^{13}C 203.5 (deshielded from **3** by 4.9 ppm) indicating slightly less charge delocalization into the naphthalene skeleton (in agreement with the 2-substitution). In addition to the cationic center, 23 more peaks were observed for the skeletal carbons. These data again suggest that **5** exists as symmetrical and unsymmetrical helical conformers (Fig. 1). The MMX calculated energy barrier between them is also high (*ca.* 85 kcal mol^{-1} using a rigid sphere model). Hence, the conformers cannot interconvert either at modest or room temperature. Quenching of **5** gave 13-(2-naphthyl)-2,3,6,7-dibenzofluorene **6** by cycloalkylation reaction. Again independent protonation of **6** in FSO_3H–SO_2ClF at −78 °C did not give any discernible protonated species ruling out any of its contamination in the ionization of **2**. Moreover quenching of **5** with water produces the starting alcohol.

Unlike **4sp** and **4ap**, the rotamers **6sp** and **6ap** (Fig. 1) cannot be separated and distinguished by NMR at room temperature. The MMX calculated rotational energy barrier between them is very low, 6–8 kcal mol^{-1}. Therefore it is suggested that the rotamer interconversion of **6** is rather fast in solution at ambient temperature.

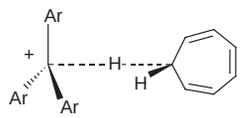
Interestingly, quenching of **5** in HBF_4 in ether with cycloheptatriene clearly gave tris(2-naphthyl)methane **7a** in 90%



5 **7a** X = H; **7b** X = D

Scheme 3

yield. This indicates less steric hindrance in **5** compared to **3** for the approach needed for hydride abstraction. Furthermore, upon treatment with perdeuterium labeled cycloheptatriene, cation **5** gave monodeuterated **7b** which was characterized by ^1H and ^2H NMR as well as mass spectrometry. This experiment proves that the methine hydrogen of **7a** comes directly from cycloheptatriene. In order to better understand the nature of the hydride abstraction, we also measured the kinetic deuterium isotope effect by treating **5** with an equimolar mixture of cycloheptatriene and cycloheptatriene-d_8. Analysis of the product mixture by ^1H NMR revealed $k_H/k_D = 7.1 \pm 0.5$. This large primary isotope effect[10] supports the colinear nature of the hydride transfer reaction and is in accord with Karabatsos' studies on the related hydride transfer of triarylmethanes.[11]



Experimental

All melting points are uncorrected. The NMR spectra were recorded on a 200 MHz NMR spectrometer. Chemical shifts are given in ppm. Mass spectra were recorded using a Finnigan Incos-50 GC-MS instrument. FT-IR spectra were obtained with a Perkin-Elmer 1550 spectrometer. The molecular mechanics calculations were carried out with PC Model 4.3, Serena Software.[8]

Preparation of tris(1-naphthyl)methanol 1

To a stirred suspension of lithium powder (40 mmol) in dry ether (10 ml), a solution of 1-naphthyl bromide (40 mmol) in dry ether (30 ml) was added dropwise. The mixture reacted exothermically and refluxed spontaneously. After the addition was complete, the mixture was refluxed for another 0.5 h, generating a dark blue solution. The mixture was then cooled to −78 °C and 1-naphthoyl chloride was added dropwise without solvent. The mixture was refluxed for 10 min, and then poured into ice–water. The organic layer was dried ($MgSO_4$), filtered, and evaporated. The residual solid was purified by column chromatography on silica gel (2 : 1 hexane–CH_2Cl_2). Crystallization from carbon tetrachloride gave **1** as white solid (50% overall), mp 218–219 °C. δ_H($CDCl_3$–TMS) 4.35 (s, 1H), 7.05–8.26 (m, 21H). δ_C($CDCl_3$–TMS) 87.6, 124.5, 125.2, 125.4, 128.6, 128.9, 129.0, 129.3, 131.6, 135.2, 141.7. IR (KBr): 3609, 3087, 3045, 1635, 1618, 1598, 1577, 1559, 1541, 1522, 1507, 1005, 782, 777 cm^{-1}; MS: *m/e* = 410 (M^+). Analysis, Found: C, 90.45, H, 5.46%; $C_{31}H_{22}O$, Calc.: C, 90.70, H, 5.40%.

Preparation of tris(2-naphthyl)methanol 2

The procedure used was the same as for **1** except that 2-naphthyl bromide and 2-naphthoyl chloride were used. Yield: 56%, mp 217–218 °C. δ_H($CDCl_3$–TMS) 2.91 (s, 1H), 7.47–7.92 (m, 21H). δ_C($CDCl_3$–TMS) 82.6, 126.2, 126.3, 126.4, 126.6, 126.8, 127.5, 127.9, 128.5, 132.6, 132.8, 143.8. IR (KBr): 3469, 3053, 2926, 1599, 1273, 1120, 821, 798 cm^{-1}. MS: *m/e*: 410 (M^+). Analysis, Found: C, 90.37, H, 5.70%; $C_{31}H_{22}O$, Calc.: C, 90.70, H, 5.40%.

Preparation of tris(1-naphthyl)methyl cation 3

To a 5-mm NMR tube containing a cold (−78 °C) mixture of **1** (40 mg) in SO_2ClF was slowly added a cold (−78 °C) solution of FSO_3H in SO_2ClF. The ^{13}C NMR spectrum was recorded at −40 °C, using capillary acetone-d_6 as the deuterium lock, as well as the reference. δ_C 124.2 (d), 124.7 (d), 125.7 (d), 126.4 (d), 126.7 (d), 128.3 (d), 128.5 (d), 128.9 (d), 129.8 (d), 129.9 (d), 130.2 (d), 130.3 (d), 130.8 (d), 131.0 (d), 131.5 (s), 133.5 (s), 133.7 (s), 134.1 (s), 134.3 (s), 136.7 (s), 141.7, 142.6 (s), 142.7 (s), 142.9 (s), 143.4 (d), 144.4 (d), 146.6 (d), 146.2 (d), 146.6 (d), 198.6 (s).

Preparation of tris(2-naphthyl)methyl cation 5

The procedure used was similar to that of **3** except that **2** was used. δ_C 128.0 (d), 128.4 (d), 128.6 (d), 129.4 (d), 129.6 (d), 131.9 (d), 132.1 (s), 132.3 (s), 132.4 (s), 133.0 (d), 134.2 (d), 134.6 (d), 136.9 (s), 137.6 (s), 138.0 (s), 138.2 (s), 138.5 (s), 138.7 (s), 139.0 (s), 148.2 (d), 148.3 (d), 149.0 (d), 149.4 (d), 203.5 (s).

Preparation of 4

A cold (−78 °C) solution of **3** in FSO_3H–SO_2ClF prepared as above was warmed to −20 °C and quenched by plunging it into ice–water. After workup, an isomeric mixture of 13-(1-naphthyl)-1,2,7,8-dibenzofluorene (**4**) was obtained as white solid, yield 98%, mp 236–238 °C. δ_H($CDCl_3$–TMS) 5.70 (s, 1/4 H), 6.08 (s, 3/4 H), 6.47–8.04 (m, 19H). δ_C($CDCl_3$–TMS) 47.0, 57.0, 118.5, 118.6, 123.0, 123.6, 124.1, 125.0, 125.5, 125.6, 125.7, 126.0, 126.2, 126.5, 127.0, 127.1, 128.3, 128.5, 128.7, 129.0, 129.9, 130.1, 130.6, 131.2, 131.8, 133.3, 133.4, 134.4, 137.1, 138.6, 139.4, 143.3, 146.4. IR (KBr): 3053, 3010, 1696, 1622, 1591, 1577, 1560, 1517, 1467, 1436 cm^{-1}. MS: *m*/*e*: 392 (M^+), 265, 188. Analysis, Found: C, 94.64, H, 5.26%; $C_{31}H_{20}$, Calc.: C, 94.86, H, 5.14%.

Quenching cation 3 with aqueous sodium hydroxide

A cold (−78 °C) solution of **3** in FSO_3H–SO_2ClF prepared as above was quenched with 20% aqueous sodium hydroxide. The resulting mixture was stirred at −20 °C for 30 min and warmed to room temperature. After workup, **1** and **5** were isolated in 32 and 56% yield, respectively.

Preparation of 6

To a cold (−20 °C) suspension of **2** (41 mg, 0.1 mmol) in diethyl ether (5 ml) was added dropwise 10 drops of 50% HBF_4 ether solution. The resulting dark blue mixture was stirred at −10 °C for 30 min, then warmed to room temperature. The characteristic blue color vanished in 2 h. After workup, 13-(2-naphthyl)-2,3,6,7-dibenzofluorene **6** was isolated as white solid, yield 100%, mp 222–224 °C, δ_H($CDCl_3$–TMS) 5.33 (s, 1H), 6.78–8.85 (m, 19H). δ_C($CDCl_3$–TMS) 56.0, 123.0, 125.0, 125.7, 126.1, 126.2, 127.1, 127.6, 127.7, 127.9, 128.3, 128.6, 128.8, 128.9, 132.7, 133.3, 134.3, 137.8, 137.9, 147.6. IR (KBr): 3050, 1690, 1610, 1570, 1425 cm^{-1}. MS: *m*/*e*: 392 (M^+), 293, 265. Analysis, Found: C, 94.70, H, 3.31%; $C_{31}H_{20}$, Calc.: C, 94.86, H, 5.14%.

Preparation of tris(2-naphthyl)methane 7a

To a cold (−40 °C) suspension of **2** (41 mg, 0.1 mmol) in acetic anhydride (2 ml) were added two drops of 48% aqueous HBF_4 solution. The resulting deep blue mixture was treated with cycloheptatriene (0.15 mmol). The stirred mixture was kept at −10 to 0 °C until the characteristic blue color of tris-(2-naphthyl)methyl cation **5** vanished and precipitation of tropylium fluoroborate commenced in 1 h. After workup, tris-(2-naphthyl)methane (**7a**) was obtained as white solid (36 mg), yield 90%, mp 56–58 °C. δ_H($CDCl_3$–TMS) 6.03 (s, 1H), 7.37–7.85 (m, 21H). δ_C($CDCl_3$–TMS) 57.2, 125.8, 126.1, 127.6, 127.9, 128.0, 128.1, 128.2, 132.3, 133.5, 141.2. IR (KBr): 3048, 1620, 1600, 1504 cm^{-1}. MS: *m*/*e*: 394 (M^+), 267, 133. Analysis, Found: C, 94.21, H, 5.80%; $C_{31}H_{22}$, Calc.: C, 94.38, H, 5.62%.

Preparation of [1-^{2}H]tris(2-naphthyl)methane 7b

The same procedure was used as for **7a** except that [1,2,3,4,5,6,7,7-$^2H_8$]cycloheptatriene[12] was used. Yield 92%, mp 57–59 °C. δ_H($CDCl_3$–TMS) 7.38–7.85 (m, 21H). δ_D($CHCl_3$–$CDCl_3$) 6.0 (s). δ_C($CDCl_3$–TMS) 125.7, 126.1, 127.6, 127.9, 128.0, 128.1, 128.2, 132.3, 133.5, 141.1. IR (KBr): 3049, 1627, 1592, 1500, 1265, 1123 cm^{-1}. MS: *m*/*e*: 395 (M^+).

Kinetic isotope effect experiment

To a cold (−40 °C) suspension of **2** (20 mg, 0.05 mmol) in acetic anhydride (5 ml) were added two drops of 48% aqueous HBF_4 solution. The resulting deep blue mixture was treated with a mixture of cycloheptatriene (5 mmol) and [1,2,3,4,5,6,7,7-$^2H_8$]cycloheptatriene (5 mmol). The stirred mixture was kept at −10 °C until the characteristic blue color of tris(2-naphthyl)-methyl cation **5** vanished. After workup, the purified mixture of **7a** and **7b** was investigated by ^{1}H NMR. The integration ratio of the nonaromatic protons to the aromatic protons was found to be 24 : 1. This translates to k_H/k_D of 7.1 ± 0.5.

X-Ray crystallography

Single crystals of compound **4sp** were obtained upon slow evaporation of an acetone solution of **4** in a 5 mm NMR tube for about one week. The X-ray data were collected at room temperature using a Nicolet/Syntex $P2_1$ diffractometer and are reported in Fig. 2.

Acknowledgements

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