

peri-Interaction between diarylmethyl and diarylmethylium units in 1,8-disubstituted naphthalenes: preference of localized structure for the C–H bridged carbocation[☆]

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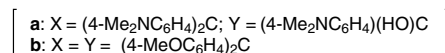
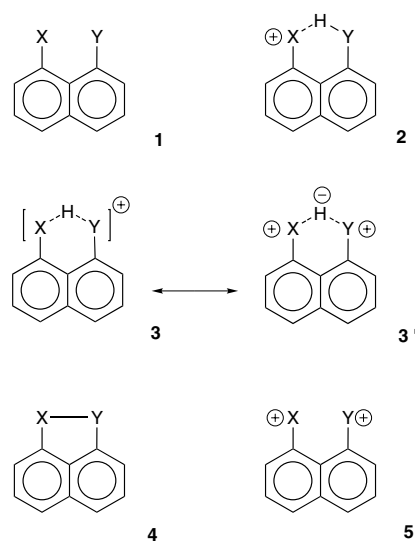
Abstract—(8-Diarylmethyl-1-naphthyl)bis(4-dimethylaminophenyl)methyliums (aryl = C₆H₅, 4-IC₆H₄, and 4-MeOC₆H₄) were generated by hydride shift from (4-dimethylaminophenyl)methyl group to the diarylmethylium unit at *peri*-positions of naphthalene. Successful isolation and low-temperature X-ray analysis indicated that they are novel C–H bridged carbocations, which prefer the localized structure with a short contact of C–H···C⁺ rather than the delocalized one with a three-centered-two-electron bond of (C···H···C)⁺.

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The naphthalene-1,8-diyl skeleton has long been attracting considerable attention in structural chemistry.¹ By providing the unique opportunity to arrange the two *peri*-substituents in a proximity, it serves as a special scaffold to investigate the attractive or repulsive interactions inbetween. A variety of 1,8-disubstituted naphthalenes have been prepared and studied in order to clarify the nature of charge-transfer interaction,² polar- π interaction,³ and π -type complexation of a Lewis acid–base pair.⁴

Another characteristic endowed by this skeleton is the cooperative enhancement of the electronic properties of the substituents, for example, Lewis basicity of ‘proton-sponge’ (**1**, X = Y = NMe₂).⁵ Chelation or formation of a three-centered bond can account for such enhance-

ment, which is also true in the 1,8-diborylnaphthalenes with strong Lewis acidity.^{6,7} In contrast to the rich chemistry for heteroatom analogues, it is still unclear whether or not the C–H–C three-centered bond⁸ would be formed at the *peri*-position of naphthalene as in **3** (X, Y = carbon substituents). It is of special interest to



Keywords: *peri*-Interaction; Carbocation; Triarylmethylium; Hydride shift; Three-centered-two-electron bond.

[☆] Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.04.002

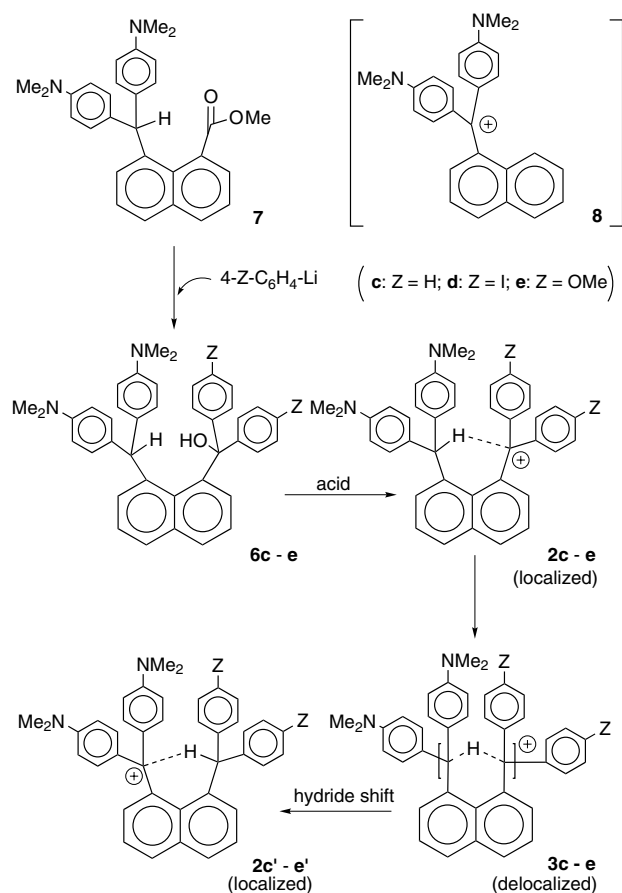
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clarify whether the C–H bridged carbocations prefer the localized structure (**2**) or the delocalized one (**3**).⁹ Very recently, we (**a**)⁴ and Gabbaï (**b**)¹⁰ postulated the involvement of the C–H bridged cations **2a,b/3a,b** as reactive intermediates during the acid-catalyzed cleavage of the long C¹–C² bond in acenaphthenes **4a,b**. In our continuing studies on the novel electrochromic systems based on the interconversion between the hexaphenylethane derivatives **4** and the naphthalenediyl dication **5** (X = Y = Ar₂C),¹¹ we have succeeded in isolating a series of diaryl(8-diarylmethyl-1-naphthyl)methylmethylums **2** [X = (4-Me₂NC₆H₄)₂C; Y = (4-ZC₆H₄)₂C; Z = H, I, OMe) for the first time. Here we report their preparation and properties as well as the precise geometrical features determined by the low-temperature X-ray analysis. Preference of the localized structure **2** over the delocalized one **3** is discussed based on the results obtained for the present system.

Diaryl(8-diarylmethyl-1-naphthyl)methanols **6** are the promising precursors¹² for the desired carbocations (Scheme 1) since the monocation could not be obtained upon treatment of the dication **5b** [X = Y = (4-MeOC₆H₄)₂C] with hydride reagents.¹⁰ The *tert*-alcohol **6c**¹⁵ containing two 4-dimethylaminophenyl and two phenyl groups was prepared by the reaction of methyl 8-[bis(4-dimethylaminophenyl)methyl]-1-naphthalene-carboxylate **7**¹⁶ with PhLi in 52% yield. Similarly, by using 4-iodo- and 4-methoxyphenyllithium were



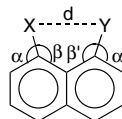
Scheme 1.

obtained **6d**¹⁵ and **6e**¹⁵ in 18% and 34% respective yield.¹⁸ The X-ray analysis¹⁹ of **6d** showed that it adopts the extended conformation with four aryl groups directed outward (Fig. S1). Yet, it still suffers from severe steric repulsion between the methine proton and hydroxy group around the *peri*-position, thus causing the in-plane deviation of substituents at C¹ and C⁸ directed outward with a largest deviation of bond angles (α, β) of 5.7° from the ideal value (120°) (Table 1).

Upon treatment of alcohols **6c-e** with HBF₄, deeply colored cationic salts were obtained in 81%, 82%, and 62% yield, respectively. On the basis of high-resolution mass spectra in a FAB⁺ mode, each cation thus obtained has the molecular formula identical to **2c-e**, respectively (Scheme 1). However, all the salts exhibit strong absorption in the same region [λ_{max} 627 (log ϵ 4.86); 629 (4.83); 628 (4.91) nm, respectively] irrespective to the substituent (Z = H, I, or OMe) at the triaryl-methanol moiety of precursors **6c-e**. The close similarity of these values to that of bis(4-dimethylaminophenyl)-(1-naphthyl)methylum **8** (627 nm) indicates that the salts in hand are not **2c-e** with the positive charge on (4-ZC₆H₄)₂C unit but have the delocalized structures **3c-e** or the hydride-shifted structures **2c'-e'**.

Further information was given by the ¹H NMR spectra in CDCl₃. Thus, the methoxy protons of **6e** (δ 3.78 ppm) and those of the corresponding salt (3.72 ppm) resonate nearly in the same region, which are not in accord with the structure **2e** for the cation. In contrast, the chemical shifts of dimethylamino groups are largely down-field shifted from **6c-e** (2.85, 2.87, and 2.85 ppm, respectively) to the salts (3.30, 3.34, and 3.30 ppm, respectively). The close similarity of the latter values to that of **8** (3.33 ppm) again indicates the considerable amount of positive charge on the (4-Me₂NC₆H₄)₂C moiety as in hydride-shifted species **2c'-e'**. In all salts, the methine proton (6.14, 6.05, and 5.99 ppm) appears in the expected region for triarylmethanes (e.g., **6c-e**: 6.56, 6.55, and 6.66 ppm, respectively). When the contribution from the delocalized structure **3** is important for these cations, the methine protons must be shifted to the far high-field since the typical values for the protons in the C–H–C three-centered-two-electron bonds are in the range of δ –3 to –7 ppm due to the resonance structure **3'** with a C⁺–H[–]–C⁺ unit.⁸ Thus, the contribution from delocalized form **3** should be marginal, if any, for the present cations, and the hydride-shifted localized structures **2c'-e'** are finally assigned to them.²⁰

In order to determine the detailed structural features, the X-ray analysis on **2c'**BF₄ was carried out at –120 °C. The single crystal contains two crystallographically independent molecules of **2c'** (mol-1 and-2), whose structures are similar to each other. As shown in Figure 1 (mol-1), the methine proton determined by Fourier Synthesis is bonded to the (C₆H₅)₂C unit (1.00 Å) in accord with the structural assignment in solution. This hydrogen is also close to the methylum carbon of (4-Me₂NC₆H₄)₂C⁺ unit. The nonbonded contact (2.26 Å) is significantly shorter than the sum of vdW radii (C···H, 2.90 Å),²¹ showing that this is one of the rare

Table 1. Listing of structural data in **6d**, **2c'** and **9c** determined by X-ray analyses at 153 K^a

Compd	α, α'	β, β'	$\Sigma(\text{C-X-C})$	$\Sigma(\text{C-Y-C})$	d (Å)
6d	117.2°, 115.7°	123.3°, 125.7°	333.9°	330.7°	3.27
2c' (mol-1)	113.8°, 117.5°	125.1°, 124.1°	359.8°	337.0°	3.02
2c' (mol-2)	112.4°, 118.0°	127.0°, 123.5°	359.6°	337.7°	3.02
9c	112.8°, 118.0°	127.0°, 122.8°	359.3°	338.1°	3.00

6d: X = (4-Me₂NC₆H₄)₂CH, Y = (4-IC₆H₄)₂COH; **2c':** X = (4-Me₂NC₆H₄)₂C⁺, Y = (C₆H₅)₂CH; **9c:** X = 4-Me₂NC₆H₄C=C₆H₄=O, Y = (C₆H₅)₂CH.

^a Estimated standard deviations of distances and angles for nonhydrogen atoms are 0.005–0.007 Å and 0.3–0.5° in **2c'**, 0.004–0.007 Å and 0.3–0.5° in **6d**, and 0.001–0.002 Å and 0.08–0.1° in **9c**, respectively.

examples of C–H bridged carbocations.⁸ The distance ratios of C···H/C–H in **2c'** (mol-1) is 2.26, which is much larger than that in the isoelectronic hydride adduct of 1,8-bis(dimethylboryl)naphthalene with a three-centered-two-electron bond (1.24).^{6a} Furthermore, as shown in Table 1, the sum of bond angles defined by C–C around the methylum carbon ($\Sigma\text{C-X-C}$: 359.8°) and the methine carbon ($\Sigma\text{C-Y-C}$: 337.0°) are close to the expected values for pure C_{sp2} (360°) and C_{sp3} of triphenylmethane (339.1° and 336.4° for two crystallographically independent molecules),²² respectively. Such geometrical features of the solid-state structure for **2c'** clearly show negligible contribution from the delocalized structure **3c**. As shown by the values of α and β in Table 1, the in-plane deviations of two substituents at C¹ and C⁸ positions in **2c'** are as large as the highly congested alcohol **6d**, suggesting that the attractive interaction through the C–H···C⁺ contact observed here is rather weak. Structural optimization of the cation by ab initio technique (B3LYP/6-31G*)²³ converged to the similar geometry to that of **2c'** in crystal (Table 2). Ab initio calculation of (8-diphenylmethyl-1-naphthyl)diphenyl-methylum **2g** indicated that the localized structure is preferred even when the substituents on the two diaryl units are identical. PM3 calculation suggested that the delocalized structure **3g** is the transition state for the degenerate interconversion of **2g**.

Finally, reactions of **2c'** with a few nucleophiles/bases were investigated. When the bridging hydrogen is abstracted as proton by the reagents, **2c'** would be

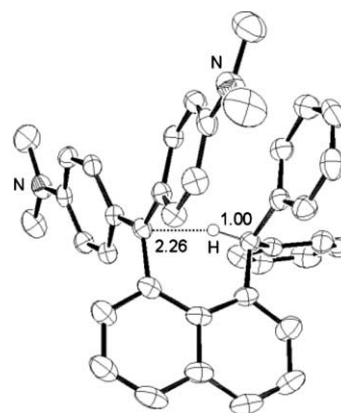
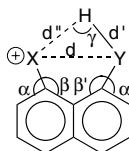


Figure 1. Molecular structure of **2c'** (mol-1) determined by X-ray analysis of BF₄[−] salt at −120 °C. The C–H···C⁺ angle is 131.2°. The C–H and H···C⁺ distances and the C–H···C⁺ angle in mol-2 are 1.10, 2.22 Å, and 127.2°, respectively.

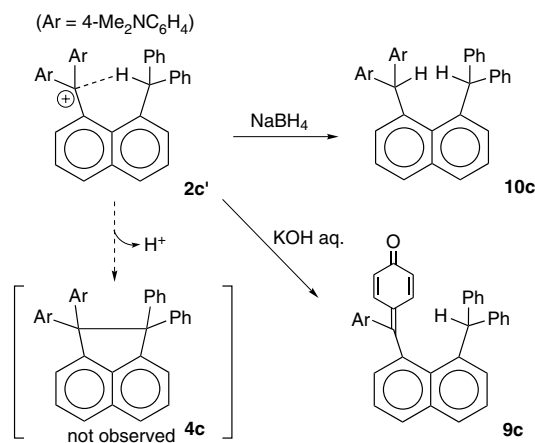
converted to the hexaphenylethane **4c** (Scheme 2); yet, this is not the case. Upon treatment of **2c'**/BF₄ with aqueous KOH was obtained quinonemethide **9c** in 75% yield, which is the hydrolyzed product of (4-Me₂NC₆H₄)₂C⁺ unit at the end group. According to the X-ray analysis of **9c** (Fig. S2),¹⁹ its geometry resembles **2c'** (Table 1). Lack of reactivity at the bridging hydrogen nor the methylum carbon may be accounted for by the sterically hindered structure of **2c'** as well as the higher steric energies for the corresponding products (e.g., **4c**

Table 2. Listing of structural data in **2c'** and **2g** calculated by ab initio technique (B3LYP/6-31G*)^a

Compd	α, α'	β, β'	γ	d, d', d'' (Å)
2c'	113.0°, 118.1°	126.4°, 123.0°	125.0°	3.15, 1.091, 2.390
2g	112.4°, 118.3°	127.2°, 123.6°	114.8°	3.20, 1.090, 2.585

2c': X = (4-Me₂NC₆H₄)₂C, Y = (C₆H₅)₂C; **2g:** X = (C₆H₅)₂C, Y = (C₆H₅)₂C.

^a Values of $\Sigma(\text{C-X-C})$ and $\Sigma(\text{C-Y-C})$ are 359.6°, 337.5° for **2c'**, and 359.8°, 338.0° for **2g**, respectively.



Scheme 2.

and the isomer of alcohol **6c**) than for **9c**. Upon treatment of **2c'**/BF₄ with NaBH₄, hydride adduct **10c** was formed as a sole product and isolated in 45% yield, which has the same skeleton to 1,8-bis[bis(4-dimethylaminophenyl)methyl]-naphthalene **10f**¹⁵ prepared from 1,8-dilithionaphthalene²⁴ and (4-Me₂NC₆H₄)₂CH⁺BF₄⁻ salt in 20% yield. Although hydride addition to the methylium carbon is quite common for triarylmethyl cations,²⁵ this result disagrees with the recent proposal by Gabbai et al.,^{10,26} who assumed that the bridged cation **2b/3b** might be converted to acenaphthene **4b** by hydride reagents.

In summary, we have succeeded in isolating and characterizing the novel carbocations with a very short C–H···C⁺ contact. The first successful X-ray analysis on the C–H bridged carbocation has proven that it prefers localized structure rather than the delocalized one with a three-centered-two-electron bond.²⁷ Studies on other C–H bridged carbocations are now underway.

Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 231949, 232245–232247. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk]. ORTEP drawings of alcohol **6d** (Fig. S1), quinonemethide **9c** (Fig. S2), and conjugate adduct **12** (Fig. S3) were submitted as electronic supplementary material.

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tem. MS spectra were measured by Mr. Kenji Watanabe and Dr. Eri Fukushi at the GC–MS & NMR Laboratory (Faculty of Agriculture, Hokkaido University).

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- Another merit of using these precursors is that C–H localized (**2**) and delocalized structures (**3**) in the isolated cationic salts would be distinguished unambiguously by X-ray analysis when two kinds of aryl substituents¹³ are placed at each of 1,8-positions (Z is not NMe₂).
- Hexaphenylethanes are notorious for giving the disordered crystal structures around the inner C–C bond due to the 'globular' molecular shape (Ref. 14). Since the carbocations **2** possess the similar structural features, there will be high possibility that the C–H···C part in **2** with four aryl groups of a kind suffers from positional disorder in crystal, thus preventing the chance to tell the localized structure from the delocalized one by X-ray analysis.
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- Selected data for new compounds are as follows. **2c'**/BF₄⁻: mp 270–275 °C (decomp.); ¹H NMR (300 MHz, CDCl₃) δ 8.12 (br d, 1H, *J* = 7.5 Hz), 7.92 (br d, 1H, *J* = 7.5 Hz), 7.51 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.48 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.21–6.98 (m, 12H), 6.68 (AA'XX', br, 4H), 6.44 (m, 4H), 6.14 (s, 1H), 3.30 (s, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 176.98, 156.64, 144.19, 140.10, 139.22, 136.88, 135.31, 134.44, 133.72, 132.82, 132.51, 129.37, 128.67, 128.04, 126.85, 126.53, 126.31, 123.99, 113.77, 53.61, 40.91; IR (KBr) 1585, 1368, 1170, 1083 cm⁻¹; UV/vis (CH₃CN) 627 (log ε 4.86), 467 (sh, 3.73), 307 (4.06) nm;

HR-MS (FAB⁺) Calcd. for C₄₀H₃₇N₂: 545.2957. Found: 545.2964. **2d**⁺BF₄⁻: mp 166.0–168.0 °C (decomp.); ¹H NMR (300 MHz, CDCl₃) δ 8.12 (br d, 1H, *J* = 7.5 Hz), 7.94 (br d, 1H, *J* = 7.5 Hz), 7.53 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.48 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.35 (AA'XX', 4H), 7.16 (br d, 1H, *J* = 7.5 Hz), 7.05 (br d, 1H, *J* = 7.5 Hz), 7.40–7.00 (AA'XX', br, 4H), 6.80–6.65 (AA'XX', br, 4H), 6.21 (AA'XX', 4H), 6.05 (s, 1H), 3.34 (s, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 175.98, 156.62, 143.43, 139.95, 137.99, 137.24, 136.58, 135.36, 134.52, 133.60, 132.54, 132.03, 131.41, 129.22, 126.96, 126.45, 124.26, 114.05, 92.02, 52.67, 41.14; IR (KBr) 2920, 1618, 1584, 1484, 1368, 1170, 1084, 1062, 1006, 940, 902, 832, 784, 728, 538 cm⁻¹; UV/vis (CH₃CN) 629 (log ε 4.83), 463 (sh, 3.80), 308 (4.16) nm; HR-MS (FAB⁺) Calcd for C₄₀H₃₅N₂I₂: 797.0890. Found: 797.0902. **2e**⁺BF₄⁻: mp 115.0–120.0 °C (decomp.); ¹H NMR (300 MHz, CDCl₃) δ 8.10 (br. d, 1H, *J* = 7.5 Hz), 7.89 (br d, 1H, *J* = 7.5 Hz), 7.50 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.47 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.20 (AA'XX', 4H), 7.15 (br d, 1H, *J* = 7.5 Hz), 7.11 (br d, 1H, *J* = 7.5 Hz), 6.69 (AA'XX', 4H), 6.37 (AA'XX', 4H), 5.99 (s, 1H), 3.72 (s, 6H), 3.30 (s, 12H); ¹³C NMR spectrum could not be measured due to its low solubility; IR (KBr) 1618, 1582, 1510, 1466, 1370, 1282, 1250, 1166, 1124, 1084, 522 cm⁻¹; UV/vis (CH₃CN) 628 (log ε 4.91), 462 (sh, 3.89), 307 (4.22) nm; HR-MS (FAB⁺) Calcd for C₄₂H₄₁O₂N₂: 605.3168. Found: 605.3155. **6c**: mp 194.0–199.0 °C (decomp.); ¹H NMR (300 MHz, CDCl₃) δ 7.75 (br d, 1H, *J* = 7.5 Hz), 7.75 (br d, 1H, *J* = 7.5 Hz), 7.34 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.23 (s, 10H), 7.19 (br d, 1H, *J* = 7.5 Hz), 7.13 (dd, 1H, *J* = 7.5, 7.5 Hz), 6.92 (br d, 1H, *J* = 7.5 Hz), 6.56 (s, 1H), 6.45 (AA'XX', 4H), 6.33 (AA'XX', 4H), 3.58 (s, 1H), 2.85 (s, 12H); IR (KBr) 3416, 1614, 1516, 1478, 1448, 1344, 1202, 1160, 1142, 1032, 820, 774, 754, 702 cm⁻¹; HR-MS (FD) Calcd for C₄₀H₃₈ON₂: 562.2984. Found: 562.2973. **6d**: mp 240.0–243.0 °C (decomp.); ¹H NMR (300 MHz, CDCl₃) δ 7.79 (br d, 1H, *J* = 7.5 Hz), 7.77 (br d, 1H, *J* = 7.5 Hz), 6.53 (AA'XX', 4H), 7.34 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.15 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.14 (br d, 1H, *J* = 7.5 Hz), 6.93 (AA'XX', 4H), 6.87 (br d, 1H, *J* = 7.5 Hz), 6.55 (s, 1H), 6.49 (AA'XX', 4H), 6.23 (AA'XX', 4H), 3.65 (s, 1H), 2.87 (s, 12H); IR (KBr) 3536, 3052, 2884, 2796, 1738, 1608, 1566, 1518, 1480, 1444, 1392, 1344, 1224, 1204, 1162, 1126, 1062, 1042, 1016, 1004, 974, 946, 824, 810, 776, 568 cm⁻¹; HR-MS (FD) Calcd for C₄₀H₃₆ON₂I₂: 814.0917. Found: 814.0940. **6e**: mp 138.0–139.5 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.74 (br d, 1H, *J* = 7.5 Hz), 7.74 (br d, 1H, *J* = 7.5 Hz), 7.34 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.22 (dd, 1H, *J* = 7.5, 1.5 Hz), 7.13 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.09 (AA'XX', 4H), 6.90 (br d, 1H, *J* = 7.5 Hz), 6.75 (AA'XX', 4H), 6.66 (s, 1H), 6.46 (AA'XX', 4H), 6.40 (AA'XX', 4H), 3.78 (s, 6H), 3.49 (s, 1H), 2.85 (s, 12H); IR (KBr) 3428, 2948, 2832, 1610, 1580, 1514, 1444, 1344, 1302, 1250, 1202, 1178, 1034, 948, 820, 798, 774, 586, 572 cm⁻¹; HR-MS (FD) Calcd for C₄₂H₄₂O₃N₂: 622.3195. Found: 622.3212. **9c**: mp 257.0–258.0 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.00 (br d, 1H, *J* = 7.5 Hz), 7.85 (br d, 1H, *J* = 7.5 Hz), 7.77 (dd, 1H, *J* = 7.5, 2.5 Hz), 7.48 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.40 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.17 (dd, 1H, *J* = 7.5, 1.5 Hz), 7.05 (m, 8H), 6.98 (dd, 1H, *J* = 7.5, 7.5 Hz), 6.59 (AA'XX', 2H), 6.54 (m, 3H), 6.48 (dd, 1H, *J* = 7.5, 2.5 Hz), 6.37 (dd, 1H, *J* = 7.5, 2.5 Hz), 6.33 (AA'XX', 2H), 5.80 (dd, 1H, *J* = 7.5, 2.5 Hz), 3.05 (s, 6H); IR (KBr) 2924, 1628, 1588, 1480, 1446, 1372, 1194, 1166, 776, 700, 534 cm⁻¹; MS (FD) *m/z* 517 (M⁺). **10c**: mp 72–73 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.76 (dd, 1H, *J* = 8.0, 1.5 Hz), 7.74 (dd, 1H, *J* = 8.0, 1.5 Hz), 7.30 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.28 (dd, 1H, *J* = 8.0, 8.0 Hz), 7.24–7.15 (m, 6H), 7.08 (dd, 1H,

J = 8.0, 1.5 Hz), 7.08 (dd, 1H, *J* = 8.0, 1.5 Hz), 6.83–6.77 (m, 4H), 6.65 (AA'XX', 4H), 6.61 (s, 1H), 6.60 (AA'XX', 4H), 6.22 (s, 1H), 2.89 (s, 12H); IR (KBr) 2922, 2852, 1611, 1517, 1492, 1347, 777, 701 cm⁻¹; HR-MS (FD) Calcd for C₄₀H₃₈N₂: 546.3035. Found: 546.3017. **10f**: mp 257–261 °C (decomp.); ¹H NMR (400 MHz, CDCl₃) δ 7.71 (dd, 2H, *J* = 8.0, 1.5 Hz), 7.28 (dd, 2H, *J* = 8.0, 8.0 Hz), 7.08 (dd, 2H, *J* = 8.0, 1.5 Hz), 6.68 (AA'XX', 8H), 6.58 (AA'XX', 8H), 6.38 (s, 2H), 2.94 (s, 24H); IR (KBr) 2880, 2792, 1612, 1518, 1346, 1224, 1200, 1160, 1132, 948, 776 cm⁻¹; MS (FD) *m/z* 632 (M⁺).

16. This ester was obtained by treatment of the corresponding carboxylic acid¹⁷ with CH₂N₂ in 69% yield: mp 147.5–148.5 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.93 (dd, 1H, *J* = 7.5, 1.5 Hz), 7.74 (dd, 1H, *J* = 7.5, 1.5 Hz), 7.56 (dd, 1H, *J* = 7.5, 1.5 Hz), 7.41 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.39 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.25 (dd, 1H, *J* = 7.5, 1.5 Hz), 6.87 (AA'XX', 4H), 6.61 (AA'XX', 4H), 6.13 (s, 1H), 3.67 (s, 3H), 2.89 (s, 12H); IR (KBr) 2948, 2888, 2804, 1718, 1614, 1518, 1480, 1446, 1346, 1278, 1228, 1196, 1164, 1144, 1076, 948, 826, 778 cm⁻¹; MS (FD) *m/z* 438 (M⁺).
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18. Many attempts to obtain pure alcohol **6f** with four 4-Me₂NC₆H₄ groups are unfruitful due to the difficulty in isolating the labile compound from the mixture containing the considerable amount of by-produced methyl *trans*-1,2-dihydro-8-[bis(4-dimethylaminophenyl)methyl]-2-(4-dimethylaminophenyl)-1-naphthalenecarboxylate **12** and methyl 8-[bis(4-dimethylaminophenyl)methyl]-2-(4-dimethylaminophenyl)-1-naphthalenecarboxylate **13**. The former is the conjugate adduct of Me₂NC₆H₄Li at the naphthalene skeleton of the ester **7**, whose structure was unambiguously determined crystallographically (Fig. S3).¹⁹ The latter seems the secondary product from **12** during aromatization by air oxidation. Low yields of **6c–e** through the reactions of **7** and 4-ZC₆H₄Li are also due to the similar by-production of such abnormal adducts.
19. Crystal data for **2c**⁺BF₄⁻: C₄₀H₃₇N₂BF₄, *M* 632.55, monoclinic, *P*2₁/*c*, *a* = 14.134 (3), *b* = 19.579 (4), *c* = 23.353 (4) Å, β = 94.054 (1)°, *U* = 6446.2 (1) Å³, *D*_c (*Z* = 8, two independent molecules) = 1.303 g cm⁻³, μ = 0.91 cm⁻¹, *T* = 153 K. The final *R* value is 0.066 for 5907 independent reflections with *I* > 3σ*I* and 835 parameters. For **6d**: C₄₀H₃₆N₂OI₂, *M* 814.55, triclinic, *P*1 bar, *a* = 9.298 (4), *b* = 9.349 (4), *c* = 20.290 (8) Å, α = 94.463 (5), β = 96.540 (4), γ = 109.370 (6)°, *U* = 1640 (1) Å³, *D*_c (*Z* = 2) = 1.649 g cm⁻³, μ = 19.53 cm⁻¹, *T* = 153 K. The final *R* value is 0.043 for 5600 independent reflections with *I* > 3σ*I* and 406 parameters. For **9c**: C₃₈H₃₁NO, *M* 517.67, triclinic, *P*1 bar, *a* = 10.847 (3), *b* = 12.742 (2), *c* = 12.809 (3) Å, α = 61.36 (1), β = 83.32 (2), γ = 64.49 (1)°, *U* = 1393.1 (6) Å³, *D*_c (*Z* = 2) = 1.234 g cm⁻³, μ = 0.73 cm⁻¹, *T* = 153 K. The final *R* value is 0.046 for 4971 independent reflections with *I* > 3σ*I* and 361 parameters. For **12**: C₃₇H₄₁N₃O₂, *M* 559.75, triclinic, *P*1 bar, *a* = 9.651 (3), *b* = 18.445 (5), *c* = 19.640 (5) Å, α = 65.55 (2), β = 73.03 (2), γ = 79.57 (2)°, *U* = 3037 (1) Å³, *D*_c (*Z* = 4, two independent molecules) = 1.224 g cm⁻³, μ = 0.76 cm⁻¹, *T* = 153 K. The final *R* value is 0.069 for 8195 independent reflections with *I* > 3σ*I* and 757 parameters.
20. Resonances of the methyl carbon in **2c**⁺ and **2d**⁺ (δ_C 177 and 176 ppm, respectively) are close to that of **8** (175 ppm), which is also in consonant with this structural assignment.
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26. Stability of cations **2c'**–**e'** under acidic conditions observed here also conflicts with their view that **2b/3b** might be unstable against acid with forming dication **5b**. We are not sure that such drastic changes in reactivity come from the different substituents on the aryl groups.
27. Similar unsymmetric structure was shown by the X-ray analysis on the hydrogen-bonded complex of a carbene with a C···H–C⁺ contact, that prefers the C–H localized structure rather than the delocalized one with a three-centered-four-electron bond Arduengo, A. J., III; Gamper, S. F.; Tamm, M.; Calabrese, J. C.; Davidson, F.; Craig, H. A. *J. Am. Chem. Soc.* **1995**, *117*, 572.