

Intramolecular triarylmethane-triarylmethylum complex: Generation, properties, and X-ray structure of a C–H bridged carbocation*

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Abstract: A series of title carbocations was generated and isolated as stable salts. X-ray analyses revealed a preference for an unsymmetric structure in which the bridging hydrogen is localized on one of the two triarylmethane units. NMR spectroscopy showed a similar preference in solution. The bridging hydrogen fluctuates between the two chromophores in solution, and the energy barrier for the H shift is linearly correlated with the C⋯C⁺ separation determined by X-ray. According to an extrapolation, the energy barrier should decrease when the C⋯C⁺ separation is less than 2.7 Å, which suggests a new model for isolable pure organic species with a three-center–two-electron bond.

Keywords: carbocation; hydride shift; isotope effects; neighboring effects; three-center bond; triarylmethylum; X-ray structure.

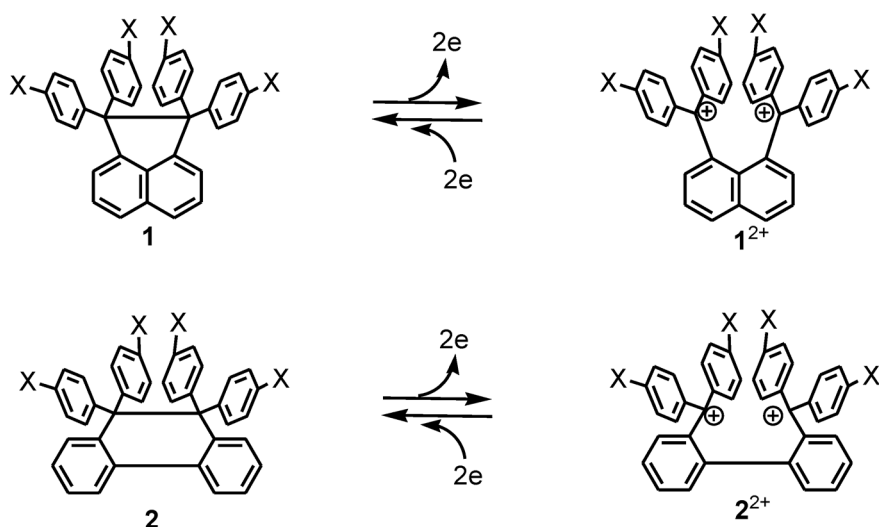
INTRODUCTION

The C–C bond length is one of the most fundamental parameters in organic chemistry [1]. A value of 1.54 Å is assumed to be the standard length of a C(sp³)–C(sp³) single bond. On the other hand, there have been several reports in which the C–C single bond is elongated [2], and these examples are often accompanied by a strained molecular structure and/or severe steric hindrance. Hexaphenylethane (HPE) is a good example of this phenomenon [3]: its central C–C bond is elongated [1.67(3) Å] primarily due to steric repulsion among the six aryl substituents.

We have been working with 1,1,2,2-tetraarylnaphthalenes **1** and 9,9,10,10-tetraaryl-9,10-dihydrophenanthrenes **2**, which can be considered as HPE derivatives [4,5]. They were originally designed as a new class of electrochromic materials based on the interconversion between arylenediylbis(diarylcarbenium)s (**1**²⁺ and **2**²⁺) accompanied by the reversible cleavage/formation of the “ethane” bond with redox reactions (Scheme 1). Based on systematic analyses of their X-ray structures at low temperature [6], they were all shown to have a C–C bond that was longer [1.614(2)–1.771(3) Å] than the standard. According to the proposed linear relationship between bond length and bond-dissociation energy (BDE) [7], a smaller BDE is expected for a longer C–C bond

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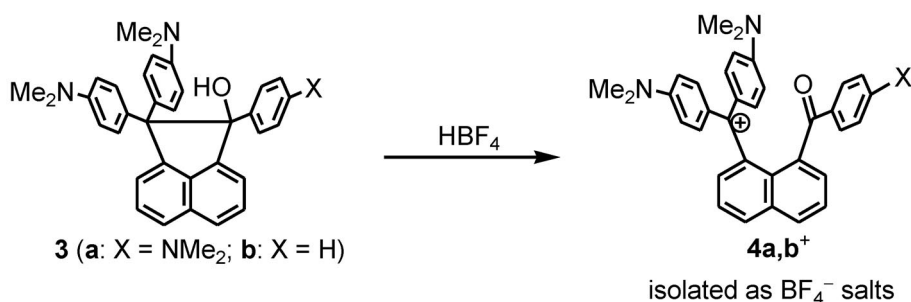
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Scheme 1 1,1,2,2-Tetraarylacenaphthenes **1** and 9,9,10,10-tetraaryl-9,10-dihydrophenanthrenes **2** are representative dynamic redox systems, which undergo reversible cleavage/formation of the long C–C bond [1.614(2)–1.771(3) Å] with redox reactions. The dicationic dyes can be isolated as stable salts to exhibit electrochromic response.

[2f,4b]. Thus, we were interested in the novel properties or reactivities associated with the cleavage of a polyarylated C–C bond.

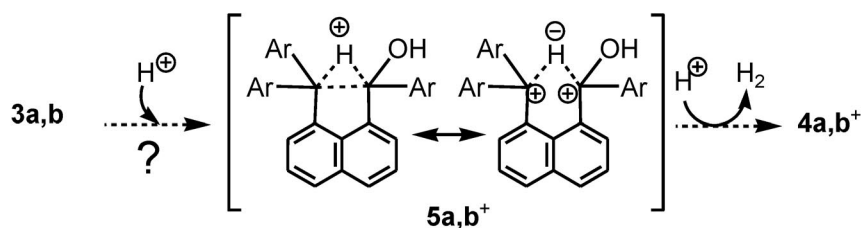
Several years ago, we encountered an intriguing case: a long C–C bond was cleaved by a Brønsted acid when 1,2,2-tris(4-dimethylaminophenyl)- (**3a**) or 1-phenyl-2,2-bis(4-dimethylaminophenyl)-1-acenaphthenol (**3b**) [1.648(4) Å] was treated with HBF_4 [8]. The products were not the expected 1,2,2-triaryl-1-acenaphthenyliums [9], but rather 8-aryloxy-1-naphthylbis(4-dimethylaminophenyl)carbeniums **4a,b⁺** where the acid-induced oxidative protonolysis of the long C–C bond accompanied by formal hydride abstraction (Scheme 2). Ketocarbeniums **4a,b⁺** were also obtained as triiodide salts upon the oxidation of **3a,b** with 3 equiv of iodine.



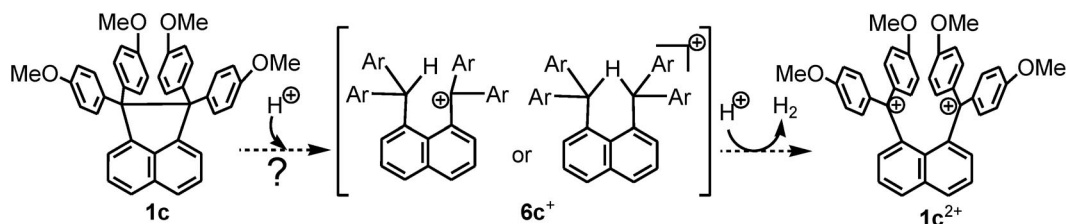
Scheme 2 Upon treatment of 1,2,2-triaryl-1-acenaphthenols **3a,b**, the products were not the expected 1,2,2-triaryl-1-acenaphthenyliums but ketocarbeniums **4a,b⁺**. Thus, the acid induced oxidative protonolysis of the long C–C bond [**3b**: 1.648(4) Å], which is less common compared to the protonolysis of a C–H bond.

Compared to the protonolysis of a C–H bond [10], C–C cleavage is less common under acidic conditions [11]. As one of the plausible reaction mechanisms, we assumed direct protonation of the long C–C sigma bond with hydrogen-bridged carbeniums **5a,b⁺** as the key intermediates in the oxida-

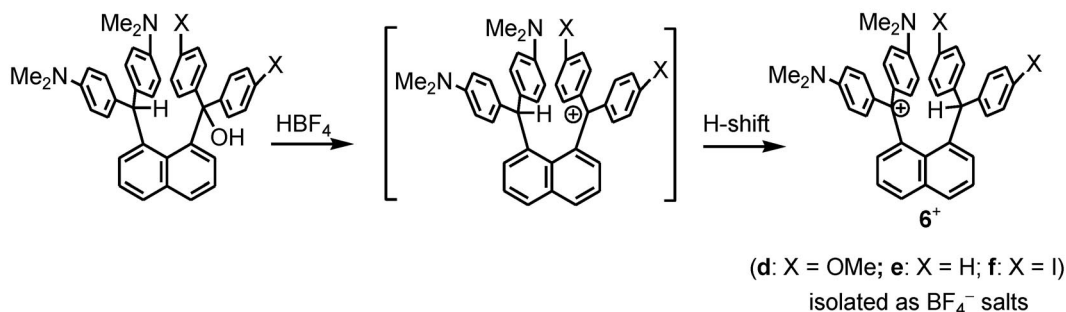
tive protonolysis of **3a,b** (Scheme 3). The structurally related tetraaryl species **6c⁺** (Ar = 4-MeOC₆H₄) with a three-center geometry was later postulated as a possible intermediate in the oxidative protonolysis of 1,1,2,2-tetraanisylacenaphthene **1c** by Gabbai and a co-worker (Scheme 4), and this was thought to be unstable under the acidic reaction conditions and spontaneously transformed into dication **1c²⁺** [12]. However, we formed a different opinion based on our results with (8-diarylmethyl-1-naphthyl)bis(4-dimethylaminophenyl)carbeniums **6d–f⁺** (X = OMe, H, I), which were generated from the carbinol precursors upon treatment with HBF₄ (Scheme 5) [13]. In contrast to the assumed instability of **6c⁺** against acid, we successfully isolated the C–H bridged carbocations **6d–f⁺** from acidic mixtures as stable BF₄[–] salts, and this should raise the question of whether these species are indeed intermediates in the oxidative protonolysis shown in Scheme 4.



Scheme 3 As one of the plausible explanations, the authors first assumed that protonated species **5a,b⁺** as the key intermediates in the oxidative protonolysis of **3a,b**.

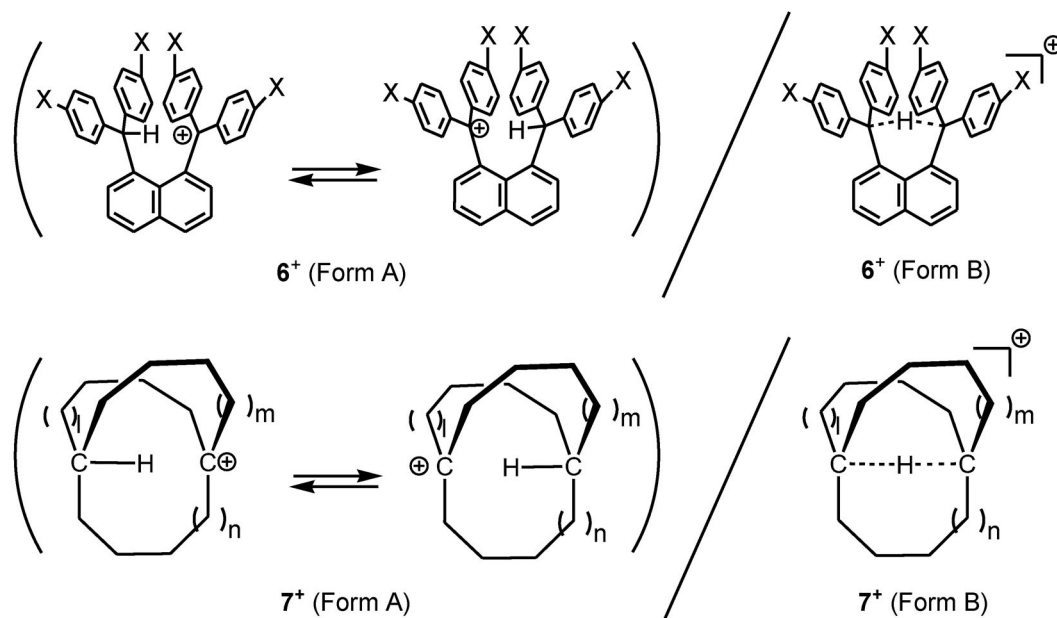


Scheme 4 The structurally related tetraarylated monocation **6c⁺** (Ar = 4-MeOC₆H₄) with a three-center geometry was later postulated as a possible intermediate in the oxidative protonolysis of 1,1,2,2-tetraanisylacenaphthene **1c** by Gabbai and a co-worker.



Scheme 5 The authors then succeeded in isolating C–H bridged carbocations **6d–f⁺** from the acidic mixtures as stable BF₄[–] salts. This should raise the question of the intermediacy of **6c⁺** in Scheme 4.

In addition to the concerns regarding stability toward acid and the intermediacy of the long-bond protonolysis, an important issue regarding these novel carbocations 6^+ is the delocalizability of the bridging hydrogen. Thus, we were interested in clarifying whether these species prefer the unsymmetric localized form that undergoes a rapid hydride shift between two triarylmethane units (6^+ , Form A) or the symmetric delocalized structure with a three-center–two-electron bond (6^+ , Form B) (Scheme 6). This issue has many things in common with carbocations 7^+ with a caged hydrocarbon framework, which have been well studied by NMR in strong acidic media by Sorensen and McMurry [14]. However, further studies on such bridged carbocations have been hampered due to their lability, which prevents their isolation to verify the geometries by X-ray analyses. In contrast to 7^+ , the title carbocations including 6^+ could be isolated as stable salts. We also thought that it would be possible to study the electronic effects (pK_R^+) of the carbocations for these species by changing the substituents on the aryl groups.



Scheme 6 The delocalizability of the bridging hydrogen is another important issue regarding the novel carbocations 6^+ : the unsymmetric localized Form A undergoes a rapid hydride shift between two triarylmethane units, whereas the Form B adopts the symmetric delocalized structure with a three-center–two-electron bond. This issue has many things in common with carbocations 7^+ with a caged hydrocarbon framework studied by Sorensen and McMurry.

In this article, we review our recent progress [15–17] on a series of intramolecular triarylmethane-triarylmethyliums. By attaching the same substituents on aryl groups/by adopting the same heterocyclic chromophores, the carbocations could adopt a (pseudo) C_2 -symmetric geometry [18]. Thus, the electronic unsymmetry of the two triarylmethane units can be minimized to study the intrinsic delocalizability of the C–H bridging unit of $[C-H\cdots C^+]$ (Form A)/ $[C\cdots H\cdots C]^+$ (Form B).

RESULTS AND DISCUSSION

Intramolecular methylacridan-methylacridinium complexes with a naphthalenediyl-type spacer $8A-C^+$

Intramolecular methylacridan-methylacridinium complexes $8A-C^+$ with a naphthalene-1,8-diyl, acenaphthene-5,6-diyl, or acenaphthylene-5,6-diyl spacer were designed as the first target molecules [15,16] (Fig. 1). They were prepared from the corresponding arylenediacrindines as shown in Scheme 7, and the TfO⁻ salts were isolated as stable crystals. The central point of this scheme is the first N-methylation of only one of the two acridine units by MeOTf, followed by hydride addition of the resulting methylacridinium unit with NaBH₄. The methylacridan-acridine precursor was then N-methylated for a second time to furnish the methylacridan-methylacridinium unit at the peri-position of 8^+ . By using NaBD₄ in the reduction step, we also obtained deuterium-bridging derivatives 8^+-d_1 , which were used to study the isotope effects for the dynamic behavior/delocalization of the bridging hydrogen. This scheme also allows selective deuterium incorporation on methyl by using MeOTf-*d*₃ for quaternization.

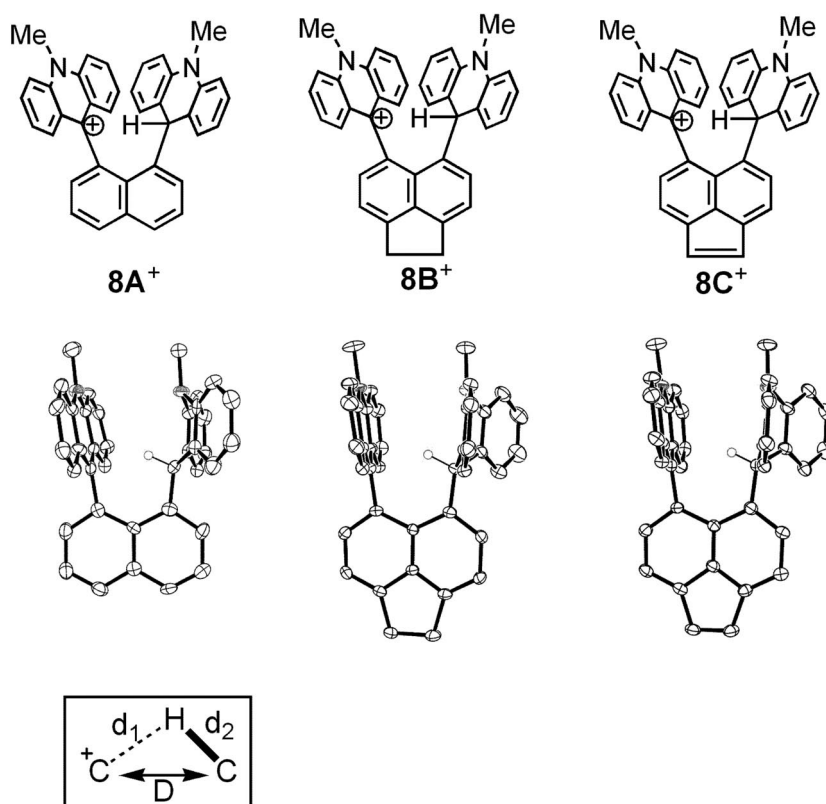
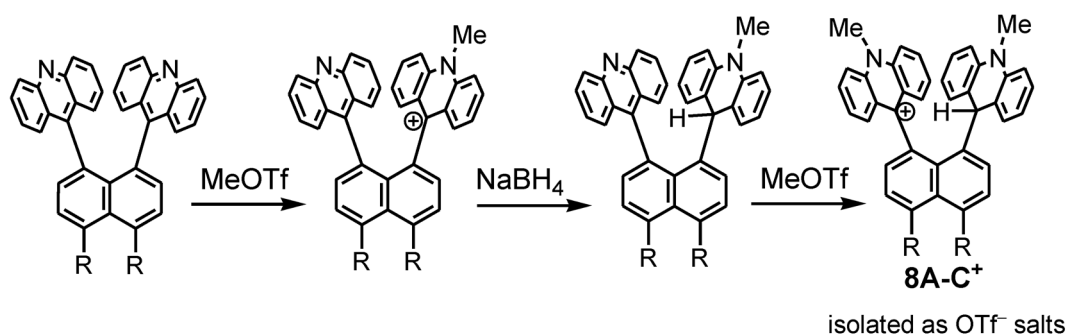


Fig. 1 Intramolecular methylacridan-methylacridinium complexes $8A-C^+$ were designed as first target, which could adopt a (pseudo) C_2 -symmetric geometry to study the intrinsic delocalizability of the C-H bridging unit of $[C-H\cdots C^+]$ (Form A)/ $[C\cdots H\cdots C^+]$ (Form B). The low-temperature X-ray analyses revealed the preference of Form A with the significant difference between d_1 (nonbonded H \cdots C⁺ distance) and d_2 (H-C bond distance) for the C-H \cdots C⁺ unit.



Scheme 7 General synthetic scheme toward the desired carbocations contains the step that differentiates the two acridine units: the first N-methylation of only one acridine unit by MeOTf, followed by hydride addition of the resulting methylacridinium unit with NaBH₄. The methylacridan-acridine precursor was then N-methylated for a second time to furnish the methylacridan-methylacridinium unit at the peri-position of **8**⁺.

Low-temperature X-ray analyses of these salts clearly show that they all prefer the unsymmetric localized structure (Form A) in crystal form (Fig. 1). There is a considerable difference between the distances (d_1 and d_2) to the bridging hydrogen from each of the C9 carbons of the two chromophores. Furthermore, one of the two chromophores is the butterfly-shaped methylacridan with C(sp³) for C9, whereas the other unit is a planar methylacridinium. The ethano or etheno bridge at the opposite peri-positions in **8B,C**⁺ enlarges the C9...C9⁺ separation (D) by increasing the pulling force at the 5,6-positions [5,19] (Table 1). These structural features as well as the difference among **8A**—C⁺ were well reproduced by DFT calculation (B3LYP/6-31G*).

Table 1 Listing of geometrical parameters^a in **8A**—C⁺ determined by X-ray analyses of OTf⁻ salts and those estimated by calculation (B3LYP/6-31G*).

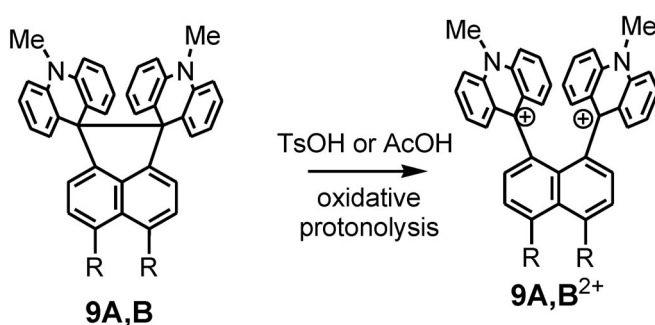
		$D/\text{\AA}$	$d_1/\text{\AA}$	$d_2/\text{\AA}$	θ/degree^b
8A ⁺	X-ray	2.951(9)	2.12(5)	0.97(6)	158(4)
	Calc.	2.999	2.047	1.102	142.7
8B ⁺	X-ray	3.004(4)	2.13(3)	1.03(3)	140(2)
	Calc.	3.008	2.148	1.102	141.6
8C ⁺	X-ray	3.031(4)	2.19(3)	0.99(4)	141(3)
	Calc.	3.110	2.170	1.102	141.6

^a D : nonbonded C...C⁺ distance; d_1 : nonbonded H...C⁺ distance; d_2 : H—C bond distance for the C—H...C⁺ unit.

^b θ : angle for C...H—C atomic array.

To confirm that a similar localized structure is also favored in solution, variable-temperature (VT) NMR analyses were conducted on these salts. Although the spectrum is for the C_{2v}-symmetric species at ambient temperature, it became C_s-symmetric with a decrease in temperature, indicating that higher symmetry is attained by the facile 1,5-hydride shift (H shift) in the unsymmetric structure of Form A, which is retarded at low temperature or suppressed in the crystal. The energy barrier (ΔG^\ddagger) for the 1,5-H shift was estimated from the coalescence temperature, and the values of ΔG^\ddagger were determined to be 10.1 and 10.9 kcal/mol for **8B,C**⁺, respectively. These values are larger than that for **8A**⁺ (<8 kcal/mol) with smaller C...C⁺ separation (D : 2.95 Å for **8A**⁺, 3.00 Å for **8B**⁺, 3.03 Å for **8C**⁺, respectively). Since only marginal primary isotope effects ($k_H/k_D = \text{ca. } 2.5$) were observed in **8A**—C⁺- d_1 , the tunneling effects are not important for the 1,5-H/D shift at the bridge.

The structurally related HPEs **9A,B** with two spiro units are very strong electron donors, and were transformed into the corresponding bis(methylacridinium)s **9A,B**²⁺ upon electrolysis accompanied by C–C bond cleavage [4a,5a]. As shown in Scheme 8, similar C–C cleavage to transform into the corresponding dications occurred when **9A** or **9B** was treated with TsOH or AcOH, respectively. The bridged carbocations **8A,B**⁺ might be considered intermediates in the oxidative protonolysis of the long-bonded HPE compounds **9A,B**. However, when the time course of oxidative protonolysis was followed by NMR spectroscopy, no resonances assignable to the bridged carbocations **8A,B**⁺ were observed at all. By considering that **8A,B**⁺ are stable and remain unchanged under the similar acidic conditions, we can safely conclude that **8A,B**⁺ are not the intermediates of oxidative protonolysis [20]. Since the reactivities of **9A,B** were suppressed under degassed conditions, it is most likely that molecular oxygen acts as an oxidant, and its oxidizing rate is increased by the protonation of O₂^{•-} [21].



Scheme 8 The structurally related acenaphthenes **9A,B** with two spiro acridan units are very strong electron donors, which are transformed into the corresponding bis(methylacridinium)s **9A,B**²⁺ upon two-electron oxidation accompanied by C–C bond cleavage. The similar C–C cleavage to the corresponding dications occurred when **9A** or **9B** was treated with TsOH or AcOH, respectively.

The above results show that the methylacridan-methylacridinium complexes **8A–C**⁺ are sufficiently stable toward acid, and thus are not intermediates of the oxidative protonolysis of long-bond compounds **9A–C**. The novel carbocations prefer an unsymmetric structure with the bridging hydrogen located on one of the two chromophores and fluctuating between them in solution.

Intramolecular methylacridan-methylacridinium complexes with a biphenyl-2,2'-diyl-type spacer **8D–G**⁺

To gain the insights into the structure–property relationship in terms of delocalizability, another series of bridged carbocations **8D–G**⁺ with a biphenyl-diyl-type arylene spacer were designed with the same methylacridan-methylacridinium substructure as **8A–C**⁺ [17]. These carbocations were chosen as the second target molecules in the anticipation that the bridging geometry could be finely tuned by putting the substituents at the bay region (**8G**⁺) or by annulation of another ring (**8D,E**⁺) on the biphenyl unit in **8F**⁺.

The dihedral angles (ϕ) of the biphenyl moiety in **8D–G**⁺ were determined experimentally by X-ray analyses of TfO⁻ salts (Fig. 2). The value is smallest in the phenanthrene-5,6-diyl derivative (**8D**⁺) and largest in the 6,6'-dibromobiphenyl-2,2'-diyl derivative (**8G**⁺). The X-ray data provided more detailed information on the bridging geometry. As in the case of **8A–C**⁺, all of the newly generated carbocations prefer the unsymmetric localized structure, and the smaller twisting angle (ϕ) corresponds to the shorter C...C⁺ separation (D).

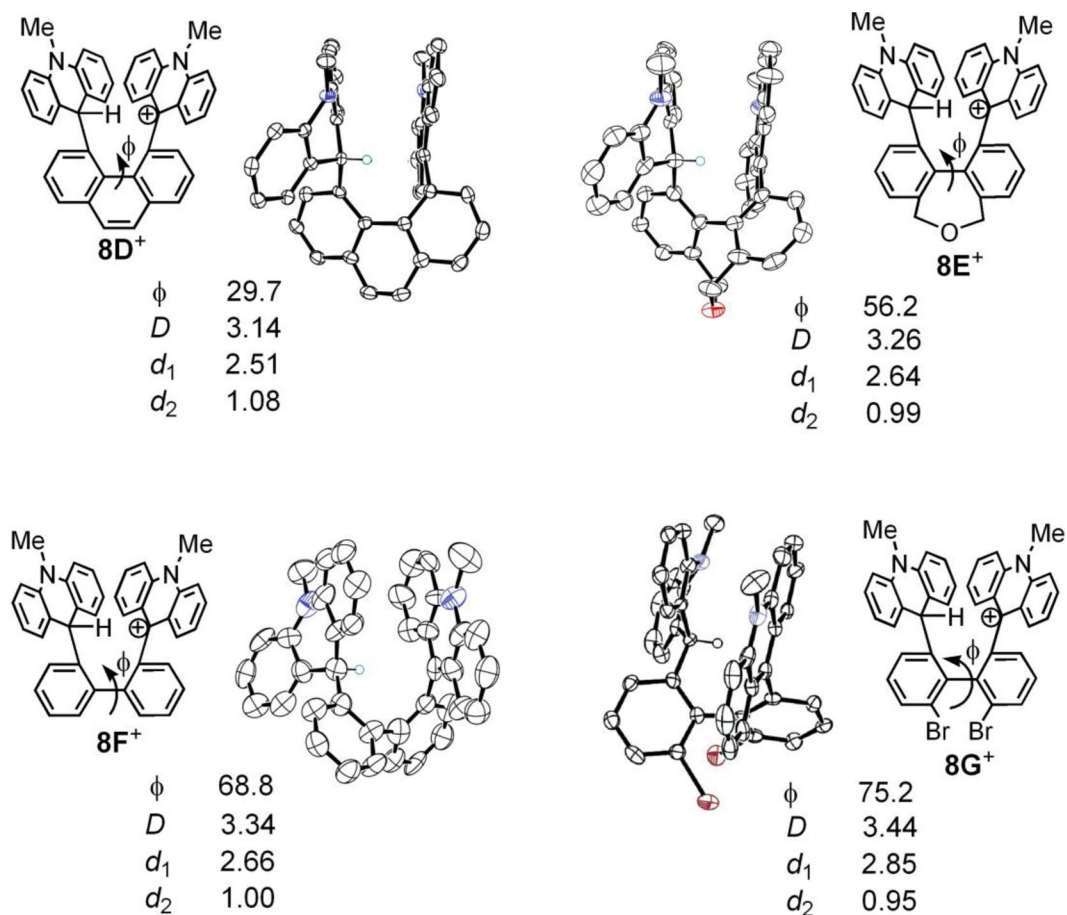
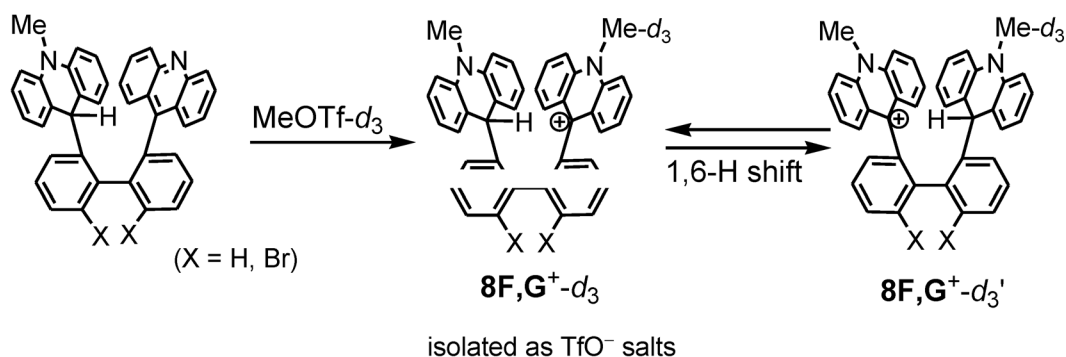


Fig. 2 Another series of bridged carbocations **8D**–**G**⁺ with a biphenyldiyl-type arylene spacer were designed with the same methylacridan-methylacridinium substructure in the anticipation that the bridging geometry could be finely tuned. The dihedral angles (ϕ) of the biphenyl moiety as well as other bridging geometries [D : nonbonded C...C⁺ distance; d_1 : nonbonded H...C⁺ distance; d_2 : H–C bond distance] in **8D**–**G**⁺ were successfully determined experimentally by low-temperature X-ray analyses of TfO[−] salts.

A similar unsymmetric localized structure is also preferred in solution, as confirmed by NMR analyses. The spectra corresponding to C_{2v} -symmetric species were observed for **8D**,**E**⁺ only at a higher temperature. The energy barriers for the 1,6-H shift were estimated to be 12.4 (**8D**⁺) and 19.2 (**8E**⁺) kcal/mol, respectively. In the case of **8F**,**G**⁺, the spectra remained uncoalesced even at 423 K, which shows that the fluctuation is much slower than the time-scale of NMR spectroscopy. Thus, the kinetics of the H shift was studied with the use of monodeuteriomethyl derivatives **8F**,**G**⁺- d_3 (Scheme 9). Based on the rate of deuteriomethyl scrambling in solution, the values of ΔG^\ddagger were estimated to be ca. 20 (**8F**⁺) and 24.6 (**8G**⁺) kcal/mol.



Scheme 9 The energy barriers for the 1,6-H shift in **8F, G⁺** are too large to be estimated by VT-NMR, so that the kinetics of the H shift was studied with the use of monodeuteriomethyl derivatives **8F, G⁺-d₃** obtained by the scheme shown here.

Based on the examination of a series of intramolecular methylacridan-methylacridinium complexes **8A—G⁺** with a variety of arylene spacers, we found a good correlation between C...C⁺ separation in the crystal (*D*) and the energy barrier of the H shift in solution (ΔG^\ddagger) (Fig. 3). If we assume a linear correlation and extrapolate, the barrier is expected to disappear when the value of *D* is less than 2.7 Å, which suggests that a delocalized form with a three-center-two-electron bond might be preferred for carbocations with a C...C⁺ separation of less than 2.7 Å.

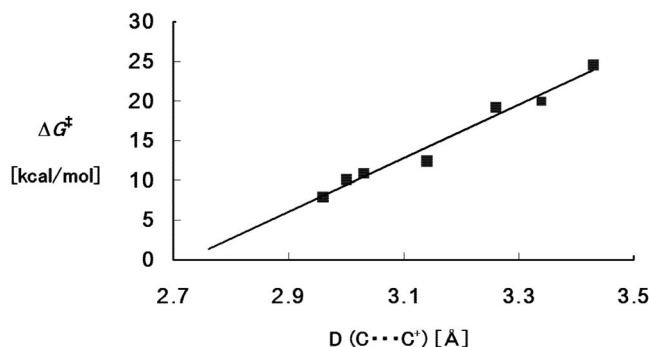


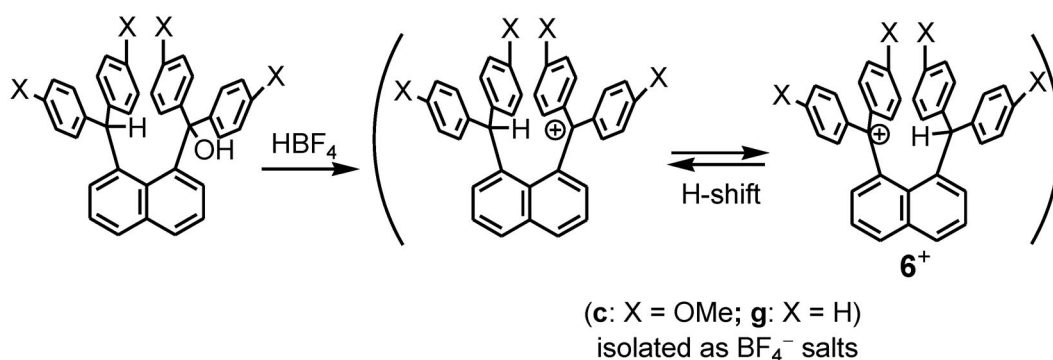
Fig. 3 Based on the examination of a series of intramolecular methylacridan-methylacridinium complexes **8A—G⁺** with a variety of arylene spacers, a good correlation was found between C...C⁺ separation in the crystal (*D*) and the energy barrier of the H shift in solution (ΔG^\ddagger). By assuming a linear correlation and extrapolate, the barrier is expected to disappear when the value of *D* is less than 2.7 Å.

Nonheterocyclic triarylmethane-triarylmethylium complexes with a naphthalenediyl spacer **6c, g⁺**

As the final targets in this article, naphthalenediyl-type bridged carbocations **6c, g⁺** with non-heterocyclic chromophores were designed to see if the electronic structure of the cationic part affects the delocalizability [16]. While tetraanisyl derivative **6c⁺** was once proposed as a reactive intermediate in the reaction of tetraanisylacenaphthene **1c** with acid [12], we were confident based on our results with **8⁺** that **6c⁺** must be stable and could be generated from the carbinol precursor under acidic conditions. Despite the much smaller pK_R^+ of the cationic subunit (−6.63 for Ph₃C⁺) [22], it would also

be possible to isolate the tetraphenyl derivative $6g^+$ thanks to stabilization of the carbenium center by C–H donation (Form A)/C \cdots H \cdots C delocalization (Form B) effects.

When diaryl(8-diarylmethyl-1-naphthyl)carbinols (Ar = 4-MeOC₆H₄, Ph) were treated with HBF₄ under dehydrating conditions, the bridged carbocations $6c,g^+$ were obtained as stable BF₄[−] salts (Scheme 10), the structures of which were unambiguously determined by X-ray analyses. They again prefer the unsymmetric localized structure (Form A) in crystal form and in solution. VT-NMR analyses proved that the bridging hydrogen fluctuates between the two triarylmethane units with an energy barrier of ca. 10 kcal/mol in both cases regardless of the pK_R^+ [−1.24 for (4-MeOC₆H₄)₂C⁺Ph] [22] of the triarylmethylium part. These results clearly show that the electronic nature does not significantly affect the rate of the H shift, and thus the delocalizability of the bridging hydrogen in 6^+ must not be affected by the pK_R^+ of the cationic subunit. This can be explained by considering that electron-donating substituents increase the C–H donating properties of the triarylmethane whereas the accepting properties of the triarylmethylium are decreased, and thus the two factors counterbalance each other.



Scheme 10 In contrast to the assumed high reactivity toward acid in Scheme 4, the bridged carbocations $6c,g^+$ were isolated as stable BF₄[−] salts by treating diaryl(8-diarylmethyl-1-naphthyl)carbinols (Ar = 4-MeOC₆H₄, Ph) with HBF₄ under dehydrating conditions.

CONCLUSION

The title carbocations were once postulated as reactive species that could be readily transformed into bis(triarylmethylium)s under acidic conditions. It was also assumed that such species might be involved as the intermediates in the oxidative protonolysis of a long C–C bond in some HPE derivatives. However, as shown here, we did not have any convincing evidence to support this notion. A series of title carbocations $6c-g^+$ and $8A-G^+$ were isolated as stable salts, and their structures were unambiguously determined by X-ray analyses.

X-ray data also revealed a preference for an unsymmetric geometry in 6^+ and 8^+ , where the bridging hydrogen is localized on one of the two triarylmethane units. NMR spectroscopy showed a similar geometrical preference in solution. The bridging hydrogen fluctuates between the two chromophores in solution, and this fluctuation is reduced at low temperature and completely suppressed in the crystal [23]. The energy barrier for the H shift is linearly correlated with the C \cdots C⁺ distance (D) determined by X-ray. According to an extrapolation, the energy barrier should diminish when D is less than 2.7 Å, suggesting that the double-well potential for the H shift in the present carbocations 6^+ and 8^+ would be changed to a single-well potential with a proper molecular design to reduce C \cdots C⁺ separation [24]. Thus, the present study enables us to propose a new isolable model for pure organic species with a three-center–two-electron bond of [C \cdots H \cdots C]⁺.

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