

Intramolecular Methylacridan–Methylacridinium Complexes with a Phenanthrene-4,5-diyl or Related Skeleton: Geometry–Property Relationships in Isolable C–H Bridged Carbocations

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Abstract: The isolation and low-temperature X-ray analyses of a series of intramolecular methylacridan–methylacridinium complexes have been achieved. The two chromophores are in close proximity due to an arylene spacer, such as a phenanthrene-4,5-diyl or biphenyl-2,2'-diyl unit. These bridged carbocations prefer the C–H local-

ized structure both in solution and in the solid state. The bridging hydrogen atom undergoes a facile intramolecular hydride shift from one carbon atom to

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another in solution, and the energy barrier is linearly correlated with the intramolecular C $\cdots$ C⁺ distance in the solid-state geometry, as determined by single-crystal X-ray analyses. By extrapolation from the data, the delocalized three-center bond of [C–H–C]⁺ would be formed when the C $\cdots$ C⁺ distance is less than 2.7 Å.

Introduction

Multicentered bonds are of interest due to their unique nature and special properties. Representative examples include the three-center two-electron (3c–2e) bond of [B–H–B], which is ubiquitously observed in uncoordinated boranes.^[1] 3c bonds in organic chemistry are much less common,^[2–4] despite the pioneering work by Sorensen, McMurry and their respective co-workers, who observed the delocalized 3c–2e bond of [C–H–C]⁺ and/or the unsymmetric C–H bridged carbocation of [C–H $\cdots$ C]⁺ in caged hydrocarbons in strong acidic media.^[5] The delocalizability of the bridging hydrogen atom in the [C $\cdots$ H $\cdots$ C]⁺ unit has been suggested to be sensitive to the geometry of the three-atom

array,^[6] which is defined by the C $\cdots$ H $\cdots$ C⁺ angle (θ), the C $\cdots$ C⁺ distance (D), and two kinds of C $\cdots$ H distances (d_1 and d_2 ; Figure 1). However, experimental verification of the geometry–delocalizability relationship has been hampered by the instability of the [C $\cdots$ H $\cdots$ C]⁺ unit, which prevents isolation for X-ray structure analyses.

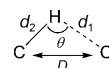


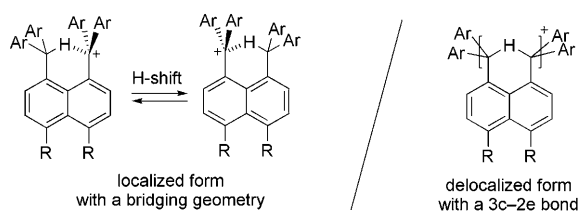
Figure 1. Geometrical parameters for [C $\cdots$ H $\cdots$ C]⁺ bridged carbocations.

In this context, our recent reports^[7] on the intramolecular triarylmethane–triarylmethyl cation complexes [Ar₃C–H $\cdots$ C⁺Ar₃] are interesting: diaryl(8-diarylmethyl-1-naphthyl)methyl cations are the first isolable C–H bridged carbocations for which the geometries have been successfully analyzed by crystallography. The central point of the molecular-design concept is the significant *peri* interaction of the naphthalene-1,8-diyl-type skeleton, which forces the two chromophores into proximity^[8] to facilitate [C–H $\cdots$ C]⁺ bridging, despite the sterically hindered triarylmethyl structure (Scheme 1). Based on an examination of several derivatives with the Ar₂C⁺ unit, such as Ph₂C⁺ and *N*-methylacridinium, it was shown that the thermodynamic stability of the cationic part (K_R^+ (methylacridinium)/ K_R^+ (Ph₃C⁺) $\approx$ 10¹⁷)^[9]

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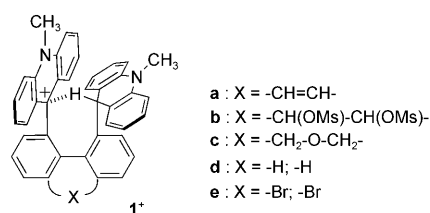
Supporting information for this article (experimental details of new-compound preparation, ORTEP drawings of **1c–f**[OTf], **2e**, and **3e**, redox behavior, and UV/Vis spectra of **1**[OTf]) is available on the WWW under <http://dx.doi.org/10.1002/chem.200801769>.



1A-C⁺: Ar₂C⁺ = *N*-methylacridinium
(A: R = H; B: R, R = CH₂-CH₂; C: R, R = CH=CH)

Scheme 1. Diaryl(8-diarylmethyl-1-naphthyl)carbeniums, the isolable intramolecular triarylmethane-triarylmethylum complexes studied previously.^[7]

does not perturb the dynamic properties of the bridging hydrogen atom. By contrast, the [C⁺⋯H⋯C]⁺ bridging distance was suggested to be a more decisive factor because the fluctuation speed of the bridging hydrogen atom in the intramolecular methylacridan-methylacridinium complexes **1A-C⁺** was altered just by replacing the acenaphthene-5,6-diyl (**1B⁺**: *D* = 3.00 Å (X-ray data); $\Delta G^\ddagger$ for hydride (H) shift = 9.6 kcal mol⁻¹ (in CD₂Cl₂) or acenaphthylene-5,6-diyl (**1C⁺**: *D* = 3.03 Å; $\Delta G^\ddagger$ = 10.1 kcal mol⁻¹) skeleton for a naphthalene-1,8-diyl unit (**1A⁺**: *D* = 2.95 Å; $\Delta G^\ddagger$ < 8 kcal mol⁻¹). To further assess the detailed relationship between the properties and the experimentally determined geometries, we planned to investigate newly designed methylacridan-methylacridinium complexes **1a-f⁺** with a variety of arylene spacers (Schemes 2 and 3), which should give a wide variety of geo-



Scheme 2. Methylacridan-methylacridinium complexes **1a-e⁺**, with a variety of arylene spacers, studied herein. Ms: methanesulfonyl.

metrical parameters for the [C⁺⋯H⋯C]⁺ bridging unit, such as different bridging distances (*D*, *d*₁, and *d*₂). Furthermore, by incorporating an arylene spacer with a flexible geometry in the complexes, we could confirm whether [C⁺⋯H⋯C]⁺ bridging provides net stabilization of carbocations **1⁺** that is more or less strong than that through π - π interactions.

The phenanthrene-4,5-diyl skeleton in **1a⁺** is a rigid arylene unit, which was used in a study of 3c-4e bonding to identify a superior "proton-sponge" analogue.^[10] On the other hand, the [C⁺⋯H⋯C]⁺ bridging distance in **1d⁺** with the biphenyl-2,2'-diyl unit must be larger than that in **1a⁺**, because **1d⁺** can adopt a skewed conformation by rotation around the biaryl axis. If the arylene unit is replaced by 9,10-dihydrophenanthrene-4,5-diyl (**1b⁺**) or 5,7-dihydrodibenz[*c,e*]oxepin-1,11-diyl (**1c⁺**) units, the skewing deformation is partly suppressed, whereas 6,6'-dibromo substitution of the biphenyl unit in **1e⁺** forces the arylene

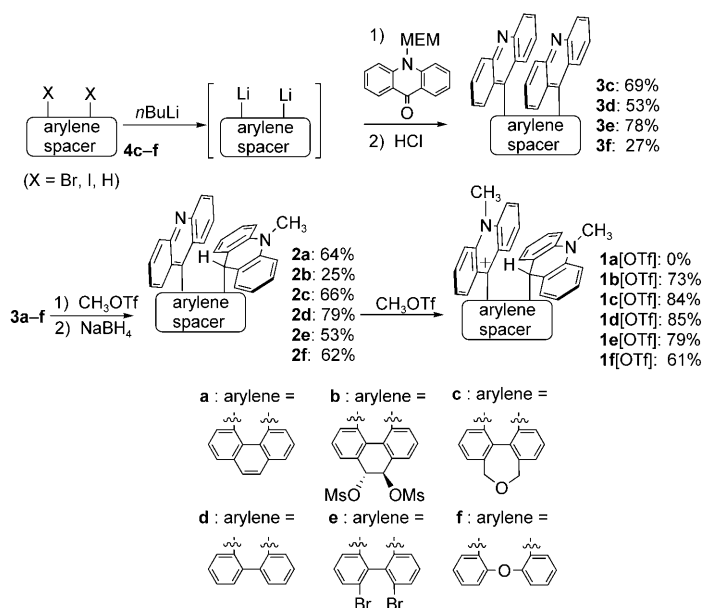
spacer to adopt a more twisted conformation than that in **1d⁺**. Methylacridan-methylacridinium complex **1f⁺**, with a diphenyl ether-2,2'-diyl unit, was also investigated; the large flexibility of the spacer in this case might induce a preference for a geometry other than the bridging one.

Herein, we report the generation and isolation of the title carbocations and their detailed structural features determined by low-temperature X-ray analyses. The bridged carbocations prefer the C-H localized structure, both in solution and in the solid state. The fluctuation behavior of the bridging hydrogen atom was studied by variable-temperature (VT) NMR spectroscopy, and a linear correlation was established between the energy barrier for the H-shift in solution and the C⁺⋯C distance (*D*) determined by crystallography.

Results and Discussion

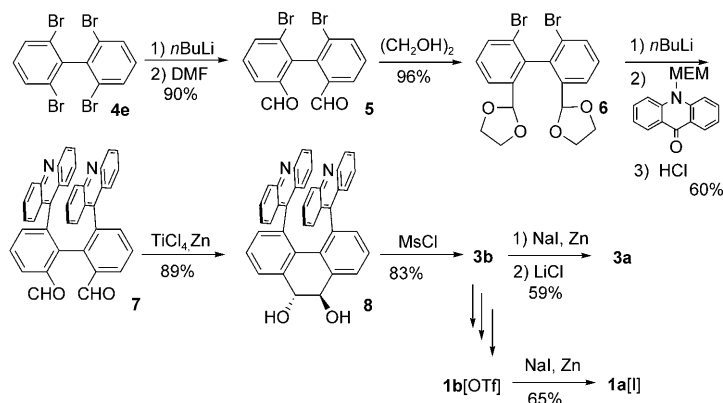
Generation and isolation of [C-H⋯C]⁺ bridged carbocations: We previously found^[7] that the naphthalene-1,8-diyl-type carbocations (**1A-C⁺**) with a [C-H⋯C]⁺ unit were generated by quaternization of the neutral precursors **2** with a methylacridan-acridine unit. Precursors **2**, in turn, were obtained from arylenedi(9-acridine)s **3** through mono-*N*-methylation with CH₃OTf followed by hydride addition with NaBH₄. Thus, we postulated that similar procedures would also work for the new series of carbocations **1a-f⁺** (Scheme 3). In fact, the less-hindered derivatives **1b-f⁺** were successfully obtained in this way.

Arylenedi(9-acridine)s **3c-f^{11,12]}** were readily obtained by the reactions of *N*-MEM-9-acridone with the corresponding dilithioarenes generated in situ by halogen-lithium exchange reactions of 1,11-dibromo-5,7-dihydrodibenz[*c,e*]oxepine



Scheme 3. Synthetic route to methylacridan-methylacridinium complexes **1b-f[OTf]**. MEM: methoxyethoxymethyl; Tf: trifluoromethanesulfonyl.

(**4c**),^[13] 2,2'-diiodobiphenyl (**4d**),^[14] and 2,2',6,6'-tetrabromobiphenyl (**4e**)^[15] or by direct deprotonation in the case of diphenyl ether **4f**^[16] (Scheme 3). Diacridines **3a** and **3b** were derived over several steps by reductive ring closure of 6,6'-diformylbiphenyl-2,2'-diyl di(9-acridine) (**7**), which was prepared from 2,2',6,6'-tetrabromobiphenyl (**4e**), as shown in Scheme 4. Diacridines **3a–f** thus obtained were smoothly converted into precursors **2a–f**. The less-hindered methylacridan–methylacridinium complexes **1b–f**⁺ were successfully generated by *N*-methylation of **2b–f** as planned (Scheme 3) and were isolated as stable OTf[−] salts.



Scheme 4. Synthetic route to hindered di(9-acridine)s **3a,b** and **1a[I]**. DMF: *N,N*-dimethylformamide.

By contrast, the most-hindered bridged carbocation **1a**⁺ could not be obtained from the methylacridan–acridine precursor **2a** under various conditions, probably because of steric hindrance. Therefore, the bridged carbocation salt **1b**–[OTf] was used as a starting material and the di(methanesulfonyloxy)dihydrophenanthrene skeleton was converted into the fully aromatized phenanthrene unit in **1a**⁺ by following the same procedure as that applied to **3b** to give **3a** (Scheme 4). To our delight, the [C–H⋯C⁺] unit in carbocation **1b**⁺ remained intact under the reductive aromatization conditions (NaI/Zn), and the desired carbocation **1a**⁺ was finally produced and isolated as a reddish-brown crystalline salt by Al₂O₃ chromatography (65% yield of **1a**[I] from **1b**–[OTf]). By counterion exchange, **1a**[OTf] could be obtained from **1a**[I]. With a series of stable carbocation salts in hand, the detailed geometrical features and dynamic properties were investigated, as described in the following sections.

Preferred geometry in the solid state (X-ray analyses):

Single crystals of **1a,c–f**[OTf] salts suitable for the X-ray analyses were successfully obtained by the vapor-diffusion method. In the case of the **1b**⁺ salt, a specimen of sufficient quality could not be obtained. Diphenyl ether derivative **1f**⁺ is labile and was gradually converted into diphenyl ether-2,2'-diylbis(*N*-methylacridinium) during the slow crystallization of the salt. The acid-promoted air oxidation of the acridan unit might be responsible for its instability, which was suppressed through addition of 1% Et₃N upon

recrystallization of **1f**[OTf]. The diffraction data were collected at low temperature so the structural parameters of carbocations **1a,c–f**⁺ were determined with sufficient accuracy. The bridging hydrogen atom was found on the D-maps. No positional disorders were observed around the [C⋯H⋯C]⁺ bridge in any case.

Regardless of the differences in the structures of the arylene spacers, one of the chromophores in **1a,c–f**⁺ is a planar methylacridinium with an sp²-hybridized C9 atom (sum of C–C–C bond angles = 359.2–360.0°), whereas the other is a butterfly-shaped methylacridan unit with an sp³-hybridized C9 atom (334.8–339.1°; Table 1). The preferred geometry of

Table 1. Geometrical parameters^[a] in methylacridan–methylacridinium complexes **1a,c–f**⁺, as determined by low-temperature X-ray analyses of OTf[−] salts, and those of related compounds (**2e**, **3e**). The optimized geometry of **1a**⁺, as calculated by DFT methods,^[b] is also shown.

	<i>D</i>	<i>d</i> ₁	<i>d</i> ₂	θ	φ	ΣC–C ⁺ –C	ΣC–CH–C
1a ⁺	3.14	2.51	1.08	116	29.7	359.2	334.8
1a ⁺ (calcd)	3.187	2.47	1.09	121	30.5	359.7	336.2
1c ⁺	3.26	2.64	0.99	121	56.2	359.8	337.8
1d ⁺	3.34	2.66	1.00	126	68.8	360.0	339.1
1e ⁺ _{mol1}	3.43	2.85	0.92	123	75.4	359.7	335.9
1e ⁺ _{mol2}	3.45	2.84	0.99	121	75.0	359.7	336.1
1f ⁺	4.89	–	1.01	–	–	359.9	337.1
2e _{mol1}	3.47	2.91	1.15	108	77.0	–	336.1
2e _{mol2}	3.56	3.04	1.11	109	75.4	–	336.0
3e	3.54	–	–	–	72.8	–	–

[a] The estimated standard deviation (esd) for *D* is less than 0.01 Å in all cases, whereas those for *d*₁ and *d*₂ are much larger (0.02–0.07 Å). [b] Conducted at the B3LYP/6-31G* level.

1a,c–e⁺ in the crystal was shown to be the structure with C–H localized bridging (observed *d*₁/*d*₂ ratio = 2.32–3.10) and not the delocalized one with a 3c–2e bond of [C–H–C]⁺ (ideal *d*₁/*d*₂ ratio = 1), as detailed below. By contrast, **1f**⁺ with a highly flexible diphenyl ether spacer does not adopt the C–H bridged geometry in the crystal, and its structure is more suitable for π–π overlapping between the methylacridan and methylacridinium units. As a result, the C9–H part of the methylacridan does not point toward the methylacridinium but rather is directed outward. The solid-state structure does not always coincide with the most stable geometry of the species due to the packing force, and this might be the case with this complex, as shown by its dynamic behavior in solution (see below). In any event, the adoption of the unbridged structure of **1f**⁺ in the crystal suggests that the stabilizing effect on the cationic moiety by the C–H bridge is comparable to that obtained by π–π overlapping (15 kJ mol^{−1} for the benzene dimer^[17]).

Among the bridged carbocations **1a,c–e**⁺, the phenanthrene-4,5-diyl derivative **1a**⁺ exhibits the closest contacts of C⋯C⁺ (*D* = 3.14 Å) and H⋯C⁺ (*d*₁ = 2.51 Å) for the [C–H⋯C]⁺ moiety (Figure 2). Due to the phenanthrene skeleton, the two chromophores are forced to be located in close proximity. However, this fused aromatic framework is less rigid than expected. A skewing deformation of the arylene spacer is noticeable, with a torsion angle (φ) of 29.7° around

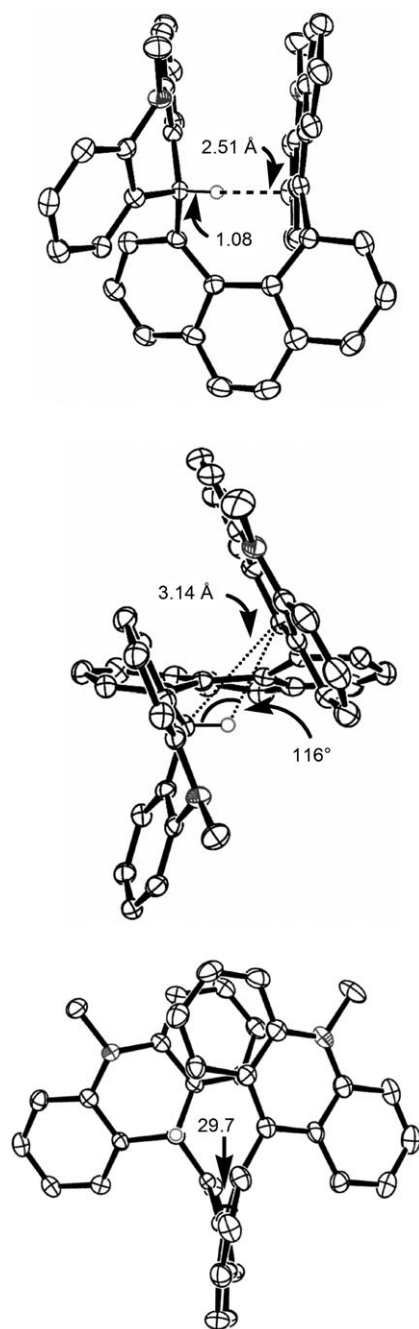


Figure 2. ORTEP drawing of methylacridan-methylacridinium complex **1a**[OTf]: a) front view; b) top view; c) side view. The counteranion and hydrogen atoms, except for the bridging one, are omitted for clarity. The negatively charged oxygen atom of the counteranion is located 3.50 Å from the C9 atom of the acridinium in the crystal.

the bay region of C4–C4a–C4b–C5, which reduces the compression effects to a lesser degree than postulated. This is the reason for the larger D and d_1 values in **1a**⁺ than in naphthalene-1,8-diyl derivative **1A**⁺ (2.96 and 2.18 Å, respectively).^[7] DFT calculations^[18] on **1a**⁺ showed that the experimentally determined geometry is well reproduced by theoretical optimization (Table 1).

As the arylene spacer becomes more skewed, the D and d_1 values gradually increase (3.26 and 2.64 in **1c**⁺; 3.34 and 2.66 in **1d**⁺; 3.43/3.45 and 2.85/2.84 Å in 2 independent molecules of **1e**⁺, respectively; Table 1 and Figures S1–S4 in the Supporting Information), which demonstrates that we can obtain a series of bridged carbocations with a wide variety of geometrical parameters for the $[\text{C}\cdots\text{H}\cdots\text{C}]^+$ bridging unit. Although no experimental data are available for **1b**⁺, it is reasonable to assume that the dihydrophenanthrene derivative has a geometry that is intermediate between those of **1a**⁺ and **1c**⁺.

X-ray analyses were also conducted on the dibromobiphenyl derivatives **2e** and **3e** (Table 1 and Figures S5 and S6 in the Supporting Information), which are the precursors of bridged carbocation **1e**⁺. These species adopt a similar twisted geometry for the arylene spacer ($\varphi = 72.8$ – 77.0°); yet, among the 3 compounds, the intramolecular separation (D) between the C9 carbon atoms of the acridine-type chromophore is smallest in **1e**⁺. Thus, the attractive nature of the short $[\text{C}\cdots\text{H}\cdots\text{C}]^+$ contact in **1e**⁺ is stronger than that of the $[\text{C}\cdots\text{H}\cdots\pi]$ -type (**2e**) or $[\pi\cdots\pi]$ -type (**3e**) interactions.

Preferred geometry in solution (VT-NMR analyses): The ¹H NMR spectrum of acridan-acridinium complex **1a**[OTf] in CD₃CN is C_{2v} symmetric at 343 K, with only one N -methyl resonance at $\delta = 3.74$ ppm, which can be assigned either to the structure with a 3c–2e $[\text{C}\cdots\text{H}\cdots\text{C}]^+$ bond (“delocalized form”) or to the unsymmetric bridged structure of $[\text{C}\cdots\text{H}\cdots\text{C}]^+$ undergoing rapid H-shift (“localized form”). When the temperature was lowered, several signals, including N -methyl peaks, became broad and split (Figure 3). At 233 K, sharp resonances appeared again with two distinct N -methyl resonances at $\delta = 4.50$ (acridinium) and 2.99 ppm (acridan), which can be explained by assuming a C_1 -symmetric structure similar to the solid-state geometry with a skewed arylene spacer.^[19] These results clearly show that the preferred geometry of **1a**⁺ in solution is also unsymmetric, with the bridging hydrogen atom localized on one of the acridine-type chromophores. In contrast to the frozen geometry in the solid state, the bridging hydrogen atom fluctuates between the two chromophores in solution. Based on the VT-NMR analysis with a T_c (coalescence temperature) of 278 K for the above-mentioned N -methyl protons at 300 MHz, the energy barrier ($\Delta G^\ddagger$) for the H-shift at the T_c value was determined to be 12.4 kcal mol^{−1}, with an error of 0.3 kcal mol^{−1} due to the uncertainty in determining the T_c value.

Similar temperature dependence was observed in the NMR spectra of **1b,c**[OTf] in [D₆]DMSO, although the coalescence of N -methyl resonances occurs at much higher temperatures ($T_c = 363$ and 423 K, respectively), which correspond to the larger values of $\Delta G^\ddagger$ ((16.4 ± 0.3) and (19.2 ± 0.3) kcal mol^{−1}, respectively, at the T_c value). As suggested by the X-ray analyses, the skewed geometry with a larger D value in **1b,c**⁺ must be the reason for their higher activation energies for the H-shift. In fact, the spectrum did not show complete coalescence even at 423 K for **1d**[OTf], the more

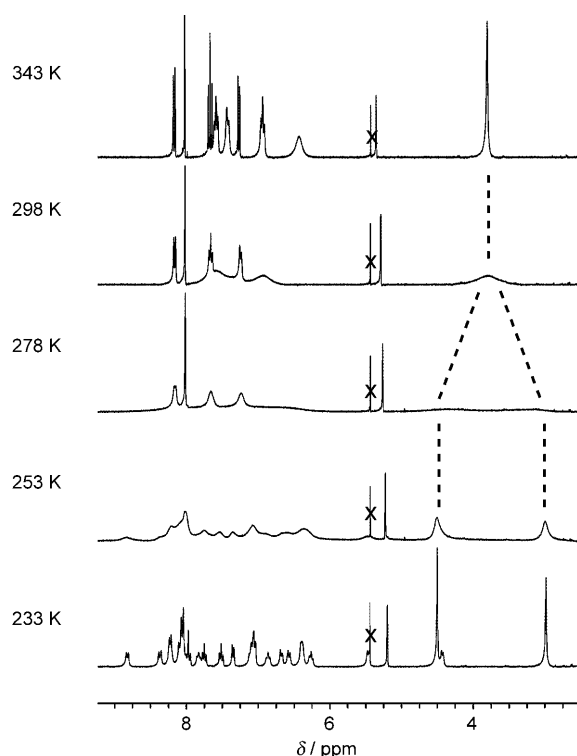


Figure 3. VT-NMR analysis of **1a**[OTf] in $[D_3]$ acetonitrile.

skewed derivative. The T_c value seems to be just above that temperature, which suggests that $\Delta G^\ddagger$ is approximately 20 kcal mol^{-1} in **1d**⁺.

For **1e,f**[OTf], the fluctuation of the bridging hydrogen atom is too slow for us to estimate its activation energy by VT-NMR spectroscopy. Thus, upon treatment of methylacridan–acridine complexes **2e,f** with CD_3OTf at room temperature, labeled carbocation salts $[D_3]1e,f[OTf]$ with deuterium atoms on the methylacridinium moiety were obtained as the primary products (Scheme 5); these slowly underwent an H-shift to give a 1:1 mixture of two isomeric $[D_3]1e,f[OTf]$ salts with deuterium atoms either on the methylacridinium moiety or on the methylacridan moiety (Figure 4). From the kinetics of deuterium scrambling ($k = 7.76 \times 10^{-5} \text{ s}^{-1}$ for **1e**⁺ and $4.65 \times 10^{-5} \text{ s}^{-1}$ for **1f**⁺ at 318 K in $[D_3]$ acetonitrile), the values of $\Delta G^\ddagger$ for the H-shift in **1e**⁺ and **1f**⁺ were determined to be 24.6 ± 0.1 and $25.0 \pm 0.1 \text{ kcal mol}^{-1}$ (318 K), re-

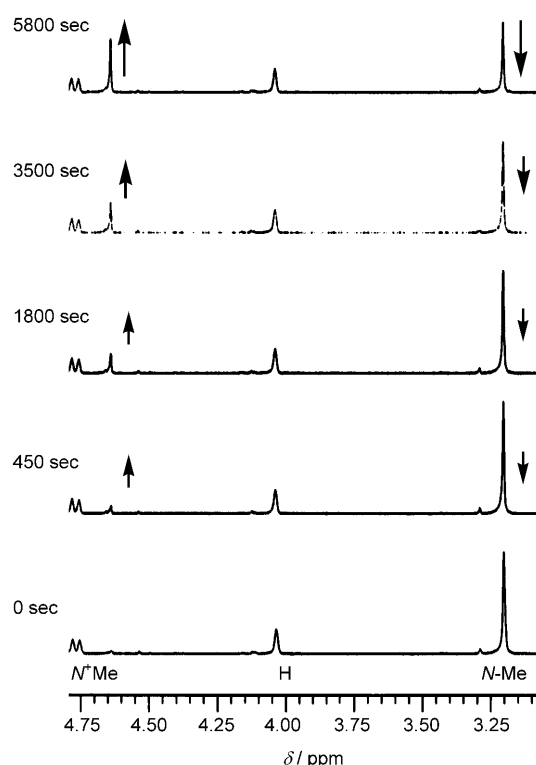
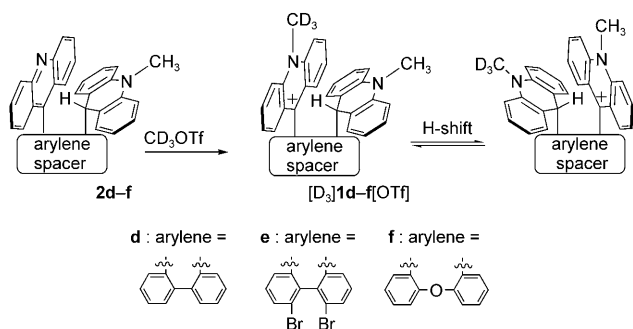


Figure 4. Deuterium scrambling of $[D_3]1e[OTf]$, as followed by 1H NMR spectroscopy in $[D_3]$ acetonitrile.

spectively; these values are much larger than those in **1a-c**⁺, as supposed. When methylacridan–acridine complex **2d** with a biphenyldiyl spacer was treated with CD_3OTf , only the isomer mixture of $[D_3]1d[OTf]$ was obtained, because the deuterium scrambling of $[D_3]1d^+$ is finished before the *N*-methylation of **2d** is complete. These results are consistent with the fact that the $\Delta G^\ddagger$ value of the H-shift in **1d**⁺ (approximately 20 kcal mol^{-1}) is smaller than those in **1e,f**⁺, as suggested by VT-NMR analyses.

The chemical shifts of the bridging hydrogen atoms for **1a-e**⁺ are in the range $\delta = 4.04\text{--}5.29 \text{ ppm}$ and are shifted up-field relative to those of the corresponding neutral precursors **2a-e** (Table 2). Although they are very different from the characteristic values for the bridging hydrogen atoms in aliphatic caged carbocations with $3c\text{--}2e$ $[C\text{--}H\text{--}C]^+$ units ($\delta = -7$ to -3 ppm),^[5,20] a less exotic value of $\delta = 2.99 \text{ ppm}$ was predicted theoretically for the delocalized $[C\text{--}H\text{--}C]^+$ unit framed in the triarylmethyl-type system.^[6b] Thus, the



Scheme 5. Preparation of $[D_3]1d\text{--}f[OTf]$ for studying the slower H-shift.

Table 2. Chemical shift (δ) values of the bridging hydrogen atoms in methylacridan–methylacridinium complexes **1a–f**[OTf] and precursors **2a–f**.

Compounds	1a–f ⁺ in $[D_3]MeCN$ [ppm]	2a–f in $CDCl_3$ [ppm]	$\Delta\delta$
1a ⁺ / 2a	5.29	5.57	–0.28
1b ⁺ / 2b	4.57	4.77	–0.20
1c ⁺ / 2c	4.25	4.58	–0.33
1d ⁺ / 2d	4.26	4.87	–0.61
1e ⁺ / 2e	4.04	4.24	–0.20
1f ⁺ / 2f	4.86	5.22	–0.36

observed upfield shifts ($\Delta\delta$) in $1a-e^+$ are indicative of the higher electron density of the bridging hydrogen atom, which is consistent with the μ -hydrido contribution for the $[C\cdots H\cdots C]^+$ bridge in the present carbocations. A similar upfield shift observed in $1f^+$ suggests that this carbocation with a flexible arylene spacer also adopts a bridging geometry, at least in part, in solution. This idea is supported by the fact that the $\Delta G^\ddagger$ value for the H-shift in $1f^+$ is similar to that in $1e^+$, which cannot be accounted for by assuming that the π - π overlapped structure in the crystal of $1f[OTf]$ is maintained in solution.

Geometry–reactivity relationship: The C–H bridged carbocations studied here are interesting not only as unique motifs for studying the organic 3c–2e bonding of $[C-H-C]^+$ but also as model intermediates for the intramolecular H-shift in carbocations,^[21,22] such as that in the Wagner–Meerwein rearrangement. We have successfully obtained the X-ray structures of a series of C–H bridged carbocations, $1a,c-e^+$, which can be considered to be snapshots of 1,6-H-shift precursors frozen in the crystalline state. Upon dissolution, the bridging hydrogen atom begins degenerate rearrangement by an H-shift. The energy barriers are in the range of 12.4 to 25.0 kcal mol^{−1} and show a linear correlation with the separation of $C\cdots C^+$ (D) in the $[C\cdots H\cdots C]^+$ unit, as determined by X-ray analyses (Figure 5). Although the solid-state

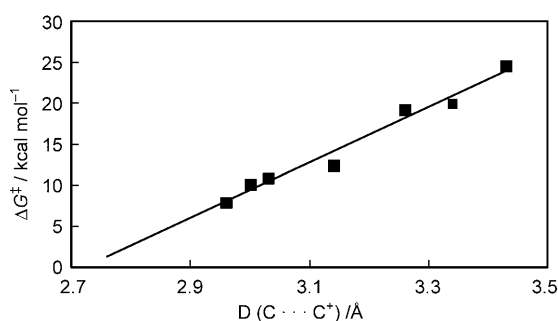


Figure 5. Linear correlation between the crystallographically determined $C\cdots C^+$ separation (D) and the $\Delta G^\ddagger$ value of the H-shift determined in solution for methylacridan–methylacridinium complexes $1a,c-e[OTf]$ and $1A-C[OTf]$.

geometry does not always represent the structure of the dominant species in solution, they must be alike for the present bridged carbocations, $1a,c-e^+$, based on a consideration of the skeletal rigidity with the congested substructures.

The regression line, which includes our previous data on $1A-C^+$, indicates that the $\Delta G^\ddagger$ value of the H-shift decreases as the $C\cdots C^+$ (D) separation in the $[C\cdots H\cdots C]^+$ unit becomes smaller (Figure 5). From an extrapolation, the energy barrier would disappear when the value of D is less than 2.7 Å. Based on an analogy with very strong intramolecular O–H $\cdots$ O hydrogen bonding (3c–4e),^[23] a delocalized single-well potential would be realized for these cases, which suggests that carbocations with pure organic 3c–2e bonding of

$[C-H-C]^+$ must be formed as isolable species by adopting a new molecular design concept for the D value to be less than 2.7 Å.

Conclusion

The present results demonstrate that intramolecular methylacridan–methylacridinium complexes $1a-e^+$ with a variety of arylene spacers can be best described as C–H bridged carbocations with a C–H localized geometry that exhibit a facile 1,6-hydride shift. Modification of the geometry of the $[C\cdots H\cdots C]^+$ unit (D , d_1 , d_2 and θ) drastically changes the dynamic behavior of the bridged carbocations. This research shows that studies on isolable C–H bridged carbocations should provide deeper insight into 3c bonds between carbon and hydrogen atoms, thanks to the finely tuneable geometry, the details of which can be determined precisely by X-ray analyses. Studies on species with much smaller $C\cdots C^+$ separation (D) are now in progress to design isolable carbocations with a delocalized 3c–2e bond of $[C-H-C]^+$.^[24]

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