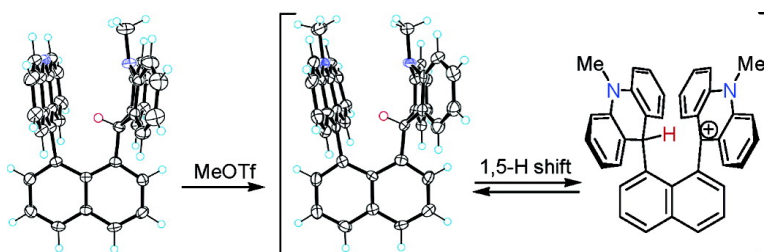## Communication

Isolation and Low-Temperature X-ray Analysis of Intramolecular Triarylmethane–Triarylmethylium Complex: Preference for a C–H-Bridged Unsymmetric Structure Exhibiting a Facile 1,5-Hydride Shift and Charge-Transfer Interaction

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Isolation and Low-Temperature X-ray Analysis of Intramolecular Triarylmethane–Triarylmethylium Complex: Preference for a C–H-Bridged Unsymmetric Structure Exhibiting a Facile 1,5-Hydride Shift and Charge-Transfer Interaction

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A carbocation with a short C–H⋯C$^+$ contact has long attracted considerable attention since the first observation of the delocalized three-center two-electron (3c–2e) bond of (C⋯H⋯C)$^+$ by Sorensen and McMurry in superacidic media.[1] From both experimental[2] and theoretical[3] perspectives, the most interesting point in studying these cations is to clarify what factors affect the preference of the localized or delocalized position of the bridging hydrogen, which should provide the key information for understanding the nature of the nontriangular 3c bond between carbon and hydrogen. Recently, the existence of a higher analogue of (C⋯H⋯C⋯H⋯C)$^+$ was theoretically predicted,[3a] and such bonding would not be stabilized in the alicyclic-bridged propellane studied before, but rather in a novel motif, triarylmethane–triarylmethylium complex,[4] where the interacting parts are geometrically constrained by being located at the *peri* positions of the rigid arylene spacer.

We envisaged that the isolable member of such triarylmethane–triarylmethylium complexes[4] would provide invaluable information on the less-explored 3c bonds in organic chemistry[5] when analyzed not only in solution but also crystallographically. We designed molecules with the general formula **A** (localized) or **B** (delocalized) as the first isolable examples of C–H-bridged carbocations with (pseudo) C_{2v}-symmetry. Since bis(*N*-methylacridinium) **2a**$^{2+}$ with a rigid naphthalene-1,8-diyl framework[6] has the shortest C$^+$⋯C$^+$ nonbonded contacts [2.927(9) Å][7] among arylenebis(triarylmethylium)s,[8] hydride insertion between the C9 carbon of acridinium units as in **1a**$^+$ should provide a unique chance[9] to study an intramolecular triarylmethane–methylium complex with a very short C⋯H contact. Acridinium is also suitable as the Ar$_2$C$^+$ unit in terms of cation stability and planar geometry. We report here the successful generation and isolation of **1a**$^+$ as well as its acenaphthene-5,6-diyl derivative **1b**$^+$ and describe their detailed structures and dynamic properties based on VT-NMR analyses as well as low-temperature crystallographic data.[10]

Half-reduction of dications **2a,b**$^{2+}$ seems to be the most direct way toward the desired cations but was found to be unsuitable for their formation.[11] At last, by careful *N*-methylation of the acridine–acridan hybrids **3a,b**,[10] we were able to isolate **1a,b**$^+$ as OTf$^-$ salts[10] in respective yields of 78 and 68% (Scheme 1). Deuterium-bridged derivatives **1a,b**$^+$-*d* were similarly obtained from **3a,b**-*d*. They were stable dark-orange crystalline materials and can be kept for months at room temperature under air. The striking stability of **1a,b**$^+$ compared with the C–F⋯C$^+$-bridged cation[8b] reported recently may be related to the higher stabilizing effect by the hydrogen bridge as well as the different pK_{R+} value of the Ar$_2$C$^+$ unit.

The ^{1}H NMR spectrum of **1b**$^+$OTf$^-$ in CD$_2$Cl$_2$ is C_{2v}-symmetric at room temperature, with only one *N*-methyl resonance at 3.94 ppm, which can be accounted for by assuming a rapid degenerated 1,5-hydride shift in Form **A** or delocalized 3c–2e bond formation as in Form **B**. With a decrease in temperature, most of the reso-

Scheme 1
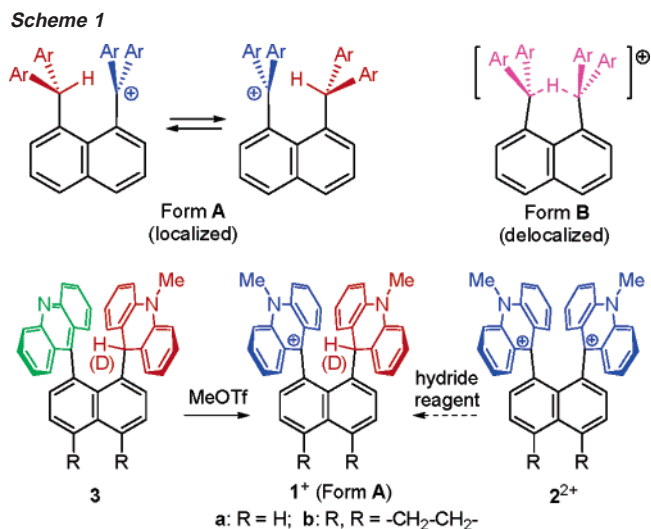
nances became broad (Figure S1).[10] A sharp C_s-symmetric spectrum appeared with two distinct *N*-methyl resonances at 4.81 (acridinium) and 3.13 (acridan) ppm (−90 °C), showing that the bridging hydrogen is localized on one of the C9 carbons in solution and fluctuates between the two equivalent sites. The chemical shift of this hydrogen is 3.90 and 4.26 ppm at 0 and −90 °C, respectively, which is close to that of precursor **3b** (4.36 ppm) but far different from the very high-field value characteristic of the delocalized 3c–2e bonding hydrogen.[2,3b] The ^{13}C NMR spectrum at −90 °C is also consistent with C_s-symmetric Form **A** and exhibits two distinct resonances for C9: 163.63 and 42.33 ppm. The ^{13}C–^{1}H coupling constant (126 Hz) is comparable to that of precursor **3b** (128 Hz), indicating full bonding character between the bridging hydrogen and one of the C9 carbons. By measuring the ^{2}H NMR spectrum of **1b**$^+$-*d*OTf$^-$, the Δδ test (^{1}H, ^{2}H) of Altman and Forsén was conducted, and the very small value (−0.02 ppm at −10 to −60 °C) clearly shows a deep double-minimum potential for the bridging hydrogen.[2,12]

The facile 1,5-hydride shift is the most characteristic process in **1**$^+$, the energy barrier (Δ$G^{\ddagger}$) of which was determined to be 9.6 kcal mol^{-1} (at T_c = −55 °C for *N*-methyl protons) for **1b**$^+$ in CD$_2$Cl$_2$ by VT-NMR analyses (300 MHz). This value is about 3-fold larger than that for the 1,5-shift in 3,7-dimethylbicyclo[3.3.1]nonan-3-yl cation.[2b] In the more polar and Lewis basic acetone-*d*$_6$, an even larger value of 10.1 kcal mol^{-1} was obtained (T_c = −43 °C), suggesting that the transition state is less polar than **1**$^+$ due to charge delocalization over the two Ar$_2$C units. The values for **1b**$^+$-*d* (10.4 kcal mol^{-1} in CD$_2$Cl$_2$; 10.7 kcal mol^{-1} in acetone-*d*$_6$) correspond to the marginal primary isotope effect (k_H/k_D = ca. 2.5), indicating that the tunneling effects are not important for the hydride shift in **1b**$^+$. The ^{1}H NMR spectrum of the naphthalene derivative **1a**$^+$OTf$^-$ exhibits essentially the same features and temperature dependence
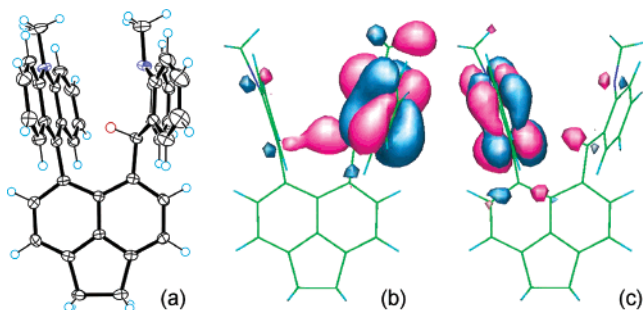
Figure 1. (a) ORTEP drawing of **1b**$^+$ in OTf$^-$ salt determined by X-ray analysis at -170 °C; (b) HOMO (-7.2908 eV) and (c) LUMO (-5.9265 eV) of **1b**$^+$ (B3LYP/6-31G*).

as that of **1b**$^+$OTf$^-$, but the much lower T_c corresponds to the smaller $\Delta G^{\ddagger}$ value (e.g., 8.4 kcal mol^{-1} for **1a**$^+$-d in acetone-d_6, T_c = -80 °C). The larger energy barrier for the hydride shift in the less flexible acenaphthene derivative **1b**$^+$ must be due to the skeletal constraint by the ethano bridge, which prevents the two Ar$_2$C units from coming closer to attain the low-energy transition-state geometry with a narrower C···C$^+$ separation. It is highly probable that the transition state for the degenerated 1,5-hydride shift of **1**$^+$ (Form **A**) adopts the geometry close to the charge-delocalized Form **B** with a shorter C···C$^+$ distance.

To investigate the detailed geometry around the bridging atoms, low-temperature X-ray analyses were carried out for both crystals of **1a,b**$^+$OTf$^-$.[10] Regardless of their different packing arrangements, one of the Ar$_2$C units is the planar acridinium with an sp^2 carbon for C9 [sum of C—C—C bond angles: 359.9(6)° for **1a**$^+$ and 360.0-(2)° for **1b**$^+$], whereas the other is the butterfly-shaped acridan unit with sp^3-hybridized C9 [342.9(6)° for **1a**$^+$ and 343.5(2)° for **1b**$^+$] (Figure 1a). The latter values are close to that found for the acridan unit in the precursor **3a** [343.0(2)°]. The geometries for the C—H···C$^+$ atomic array clearly show that the bridging hydrogen is localized on one of the C9 carbons as in Form **A** [the distances for C—H, H···C$^+$, and C···C$^+$ and the angle for C—H···C$^+$ are 0.98-(6), 2.14(6), 2.960(9) Å and 139(4)° for **1a**$^+$; and 1.03(3), 2.13(3), 3.004(4) Å and 140(2)° for **1b**$^+$, respectively]. The above geometries are the first experimental data[4a] for the interconvertible/delocalized C_{2v}-symmetric cations with (C—H···C$^+$)/(C···H···C)$^+$ contacts.

The theoretical calculation for **1a,b**$^+$ (B3LYP/6-31G*)[13] nicely reproduced the observed solid-state structure [1.102, 2.047, 2.999 Å and 142.7° for **1a**$^+$; 1.102, 2.148, 3.008 Å and 141.6° for **1b**$^+$] with two distinct Ar$_2$C units [sum of C—C—C bond angles around C9: 359.3 and 339.1° for **1a**$^+$; 359.7 and 339.1° for **1b**$^+$]. The coefficients in LUMO are mainly localized on the acridinium unit, whereas those in HOMO are on the acridan moiety (Figure 1b,c). A considerable portion of the coefficient is located on the bridging hydrogen. Although the electrochemical amphotericity of **1a,b**$^+$ is not so high [$E_{sum} = E_{ox} - E_{red} = $ ca. $+1.4$ V; $+0.90$ V (irrev.) $-$ -0.49 V (rev.) for **1a**$^+$ and $+0.81$ V (irrev.) $-$ -0.55 V (rev.) for **1b**$^+$],[10] the close proximity induces intramolecular charge-transfer (CT) interaction[6a] through the bridge. Weak, but significant, absorptions in the long-wavelength region up to 750 nm (Figures S7 and S8; log ϵ = ca. 3) are assigned to the CT absorption bands of **1a,b**$^+$, and the optically determined HOMO—LUMO gap (1.65 eV) well corresponds to those obtained by electrochemistry (ca. 1.4 eV) and by calculation (1.44 for **1a**$^+$ and 1.36 eV for **1b**$^+$). Electrochemical oxidation of the bridged cations to the dications **2a,b**$^{2+}$ occurs at a much higher potential than the corresponding arylacridans without the acridinium unit [ca. $+0.78$ V (irrev.) for **3a,b**], which must be the result of CT interaction through the

hydrogen bridge, although a Coulomb effect in the dications **2a,b**$^{2+}$ could not be completely ruled out.

These results demonstrate that the intramolecular complex of triarylmethane—methylium complexes **1** with the naphthalenediyl or acenaphthenediyl skeleton can best be described as a localized C—H-bridged cation (Form **A**),[14] with a facile 1,5-hydride shift and a significant degree of CT interaction. Adequate electron-donating properties of the Ar$_2$CH unit in **1** must play a determining role in selecting the CT-type stabilizing mode over the delocalized one in organic 3e bonds. This work suggests that studies on isolable triarylmethane—methylium complexes should keep giving deep insights into 3c bonds between carbon and hydrogen, thanks to the finely tunable electronic properties of Ar$_2$C$^+$ and Ar$_2$CH units, as well as the definable rigid geometry. Studies in this vein are now in progress.

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