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Hydrocarbon Cations

Arylbis(9-anthryl)methyl Cations: Highly Crowded, Near Infrared Light Absorbing Hydrocarbon Cations**

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Triarylmethyl cations have been widely studied since the discovery of the triphenylmethyl cation in 1901,[1,2] and highly crowded triarylmethyl cations in particular have been the subject of recent interest. Tris(1-naphthyl)methyl and tris(2-naphthyl)methyl cations (**1a** and **1b**) were synthesized as unstable species,[3] whereas the tris(1-azulenyl)methyl cations **2** were reported to be stable.[4] The arylbis(9-anthryl)methyl cations **3** should be even more highly crowded than **1** and **2**. In particular, the symmetric tris(9-anthryl)methyl cation **3f** would be a most fascinating molecule. However, none of the cations **3** have been reported.

The instability of **1a** and **1b** can be ascribed to their facile Nazarov-type cyclizations,[5] that is, a kinetic instability rather than a thermodynamic instability. Cations **3** may be less prone to undergo this rearrangement because of the doubly benzo-annelated structure of anthracene. Therefore, they would be fairly stable once formed, though the conjugation between the aryl groups might be considerably reduced due to steric congestion.

The reason for the total absence of cations **3** may be the difficulty of their synthesis. In principle, bis(9-anthryl) ketone (**4**, Scheme 1)[6,7] should be a suitable starting material. However, we found that **4** is not reactive towards organo-

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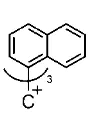
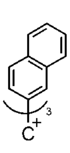


1a



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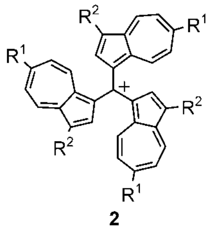

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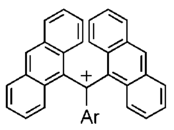
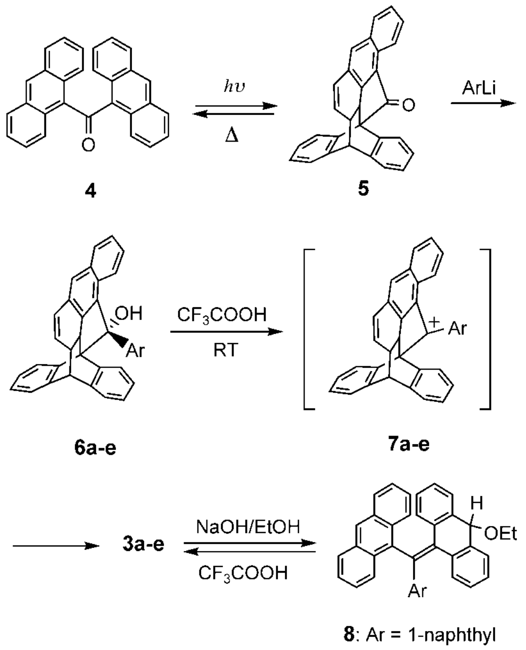


3a: Ar = phenyl
3b: Ar = *p*-tolyl
3c: Ar = *p*-anisyl
3d: Ar = 1-naphthyl
3e: Ar = 2-naphthyl
3f: Ar = 9-anthryl

metallic reagents, probably due to steric hindrance or rapid electron transfer from the reagents.[8] Thus, **4** does not afford the arylbis(9-anthryl)methyl alcohols that would be promising precursors to **3**.



Scheme 1. Synthesis of cations **3a–e** and further reaction of **3d** to **8**.

We discovered, however, that the photochemical intramolecular [4+2] cycloadduct of **4**, namely **5** (Scheme 1),[6b,9] is susceptible to nucleophilic additions. The increased reactivity of **5** comes from the following structural and electronic features: 1) It has a rigid structure, 2) one face of the carbonyl group is less hindered than the other face (according to the PM3-optimized structure), 3) the carbonyl group is less conjugated than that of **4**, and 4) its electrochemical reduction potential is about 0.35 V higher than that of **4** (−1.94 V (half-wave potential) for **5**/CH_2Cl_2/*n*-Bu_4NClO_4 vs. −1.60 V (peak potential) for **4**). Compound **5** can cyclorevert to **4** fairly easily upon heating ($E_a = 34.2 \pm 0.2$ kcal mol^{-1}; $t_{1/2} = 12.0$ h at 119 °C in [D$_5$]-bromobenzene).[10] These findings have led to a novel synthesis of **3**, which we report here.

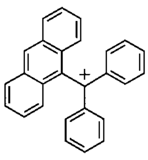
The reaction of ketone **5** with phenyllithium (3 equiv) in THF at room temperature afforded alcohol **6a** with high stereoselectivity in 82 % yield. Compound **6a** was determined to be an *exo* adduct by the observation of an NOE between the aromatic protons of the phenyl group and proton on C7 (the closest aliphatic methine proton on the bicyclo[2.2.2]octane framework, see Scheme 1). This is in agreement with the structural features of **5**. The reaction of **5** with *p*-tolyllithium, *p*-anisyllithium, 1-naphthyllithium, and 2-naphthyllithium furnished the corresponding addition products **6b** (80 %), **6c** (93 %), **6d** (51 %), and **6e** (64 %), respectively.

However, **5** still suffers from steric hindrance and attempted nucleophilic additions of the more bulky 9-anthryllithium or its Grignard reagent have been unsuccessful. The thermal cycloreversion also brought forth a problem for alcohols **6a–e**: Heating of **6a** resulted mostly in fragmentation rather than cycloreversion, probably initiated by homolytic carbon–carbon bond cleavage in the cyclopentanol moiety. The EI mass spectrum of **6a** agrees with this result, showing the molecular ion (*m*/*z* 474; 1 %) only weakly with strong fragment peaks at *m*/*z* 296 (100 %) and 178 (98 %) that correspond to the molecular weights of 9-anthryl *p*-tolyl ketone and anthracene. The considerable thermodynamic stability of the hydroxydiarylmethyl radical as well as the strain in the cyclopentanol moiety may be responsible for the preferential homolysis.

Despite the unsuccessful thermal cycloreversion of **6a**, it was found that addition of trifluoroacetic acid (TFA) to a colorless solution of **6a** in chloroform at room temperature affords the desired cation **3a** cleanly as a stable species in a deep green solution. Similarly, the tolyl, anisyl, and naphthyl compounds **6b–e** afforded the corresponding cations **3b–e** (see Scheme 1). Thus, it follows that the intermediate cations **7a–e** undergo a facile [4+2] cycloreversion at room temperature to yield the thermodynamically more stable triarylmethyl cations **3a–e** (stable for weeks in $CDCl_3$/TFA). To our knowledge, the 1-naphthyl compound **3d** is the most highly crowded triarylmethyl cation observed.

The ^{1}H and ^{13}C NMR spectra of **3** are in agreement with the cation structures.[11] For example, in the ^{1}H NMR spectrum of the *p*-tolyl compound **3b**, the signal for the proton on C10 ($\delta = 9.15$ ppm) of the anthryl groups is down-shifted by 0.75 ppm compared to the protons on C9,10 of anthracene, and the signal for the methyl protons ($\delta = 2.59$) of the *p*-tolyl group is down-shifted by 0.27 ppm compared to that of **6b** ($\delta = 2.32$). In the ^{13}C NMR spectrum, the central cation center (Cα) of **3a** is observed at $\delta = 190.97$ ($\delta = 191.84$, 187.66, 184.55, and 178.55 for **3b–e**, respectively). Thus, there is a trend of high-field shifts compared with the signal for Cα of the 9-anthryldiphenylmethyl cation **9** ($\delta = 204.11$, see below)[12,13] and the triphenylmethyl cation ($\delta = 211.56$).[13]

When a solution of **3d** in $CHCl_3$/TFA is poured into NaOH/EtOH at 0 °C, the 10-ethoxy adduct **8** is formed in 52 % yield (Scheme 1). A similar alkoxy adduct has been described for **9**.[12] When ether **8** is dissolved in $CHCl_3$/TFA, **3d** is cleanly regenerated.



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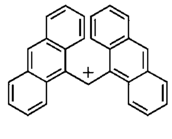

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The most remarkable feature of cations **3a**–**e** is a strong absorption in the near-infrared region ($\lambda_{max} = 855$–946 nm, band 3) in TFA (Figure 1, Table 1). There are two other absorptions in the visible region: $\lambda_{max} = 440$–470 nm (band 1) and 666–748 nm (band 2). The appearance of two bands at wavelengths longer than 500 nm contrasts with the single band of **9** ($\lambda_{max} = 786$ nm (780 nm in liquid SO_2[12])) and the bis(9-anthryl)methyl cation **10** ($\lambda_{max} = 855$ nm).[14]

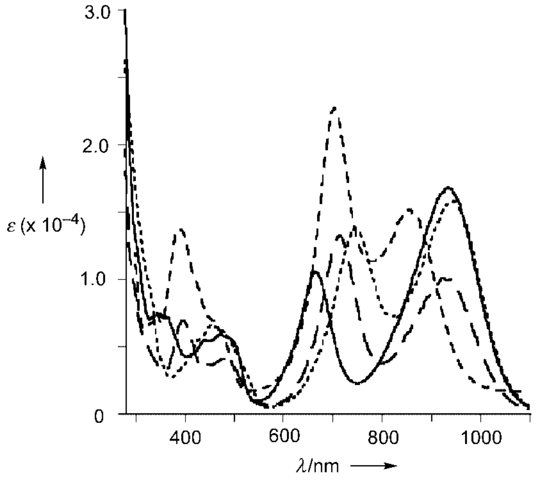

Figure 1. Absorption spectra of **3a** (solid line), **3c** (short broken line), **3d** (dotted line), and **3e** (long broken line) in CF_3COOH (ε in $M^{-1}cm^{-1}$). The absorption spectrum of **3b** is omitted for clarity (see Table 1).

Table 1: Absorption spectral data of **3a**–**e**, **9**, and **10** in CF_3COOH.

Compound	λ_{max} [nm^{-1}] ($\varepsilon \times 10^{-4}$)
3a	936 (1.68), 666 (1.06), 498 sh (0.54), 472 (0.59), 441 (0.55)
3b	916 (1.37), 681 (1.20), 496 sh (0.43), 467 (0.51), 436 (0.50)
3c	855 (1.52), 704 (2,27), 461 (0.68), 390 (1.37), 343 (0.75)
3d	946 (1.59), 748 (1.37), 456 (0.66), 421 (0.51)
3e	926 (1.03), 713 (1.35), 478 (0.42), 443 sh (0.38), 395 (0.71)
9	786 (1.14), 443 (1.18), 400 (1.62)
10	855 (2.76), 539 sh (0.29), 473 (0.85)

In the case of cations **3**, with the exception of **3c**, band 3 is at longer wavelength than the absorption of **9**, where band 2 is at even shorter wavelength than the absorption of **8**. We think that bands 2 and 3 might be associated with orbital splitting by homoconjugation between the two 9-anthryl groups. According to a semi-empirical calculation (AM1), the optimized structure of **3a** (Figure 2) takes a deep propeller conformation and there are large coefficients for the HOMO orbitals at the 9-positions of the anthryl groups with small coefficients at Cα. In this situation, it seems possible that there is some interaction (homoconjugation) between the p orbitals at the 9-positions of the anthryl groups. The dianthrylmethyl cation **10** does not adopt a propeller conformation (AM1): One anthryl group is twisted against the plane of the 9-anthrylmethyl cation and the HOMO coefficients on the twisted anthryl group are small, disfavoring homoconjugation. The idea of orbital splitting due to homoconjugation is in agreement with the small difference in wavelength between bands 2 and 3 for the *p*-anisyl cation **3c** ($\Delta\lambda = 151$ nm, compared with $\Delta\lambda = 270$ nm for **3a**) and the unusual blue shift of the longest wavelength absorption (855 nm for **3c** vs. 936 nm for **3a**). This blue shift contrasts with the appreciable red shift of the *p*-anisyldiphenylmethyl cation (476 nm) relative to the triphenylmethyl cation (431, 404 nm).[15] The larger chemical shifts of the anthryl groups of **3c** (H10: $\delta = 9.03$; C10: $\delta = 187.66$ ppm) compared to those of **3a** indicate a considerable resonance contribution of the *para*-quinoid structure of the *p*-anisyl group as usually observed. This results in a slightly better coplanarity of the molecule (AM1), which is less favorable for homoconjugation.

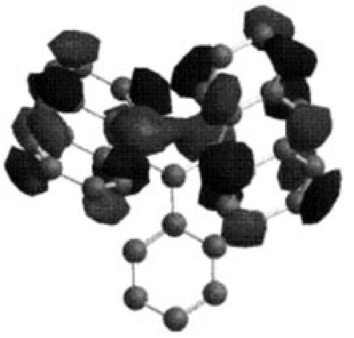

Figure 2. The HOMO orbitals of **3a** as obtained by the AM1 method. The orbital coefficients at Cα and the phenyl group are small.

In view of the stability of **3a**–**e**, the tris(9-anthryl)methyl cation **3f** should also be a stable species when once formed. Further studies on arylbis(9-anthryl)methyl cations including attempts to synthesize **3f** are under way. Transformation of **3a**–**e** to the corresponding methanes, carbanions, and radicals are also in progress.

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[7] Compound **4** has been prepared by Friedel–Crafts acylation of anthracene with 9-anthracenecarbonyl chloride in rather poor yield (21 %).[6b] We found that the oxidation of bis(9-anthryl)-methyl alcohol—readily obtainable by the reaction of 9-anthraldehyde with 9-anthryllithium—with 2,3-dichloro-5,6-dicyano-1,4-quinonediimine (DDQ) in THF at room temperature affords **4** in 95 % yield. Oxidation of the alcohol with pyridinium chlorochromate (PCC) resulted mostly in fragmentation to give 9-anthraldehyde and other compounds.

[8] Upon addition of phenyllithium to a solution of **4** in THF at −70 °C, the mixture turned deep red; compound **4** was mostly recovered after quenching with water. The electrochemical reduction potential of **4** is about 0.45 V lower than that of benzophenone ($E_{1/2} = -2.06$ V, CH_2Cl_2), which indicates a considerably higher electron acceptor ability.

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[10] The activation energy was obtained by measurement of the decrease of signal intensity for the aliphatic protons of **5** by ^{1}H NMR spectroscopy at four different temperatures.

[11] Cation **3a** showed broadening of the signals below 0 °C, which is suggestive of a dynamic process. However, the presence of TFA as the co-solvent has prevented detailed NMR measurements at low temperatures.

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