Isolation of an Antiaromatic 9-Hydroxy Fluorenyl Cation

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Dedicated to Herbert W. Roessler on the occasion of his 85th birthday.

Abstract: Fluorenyl cations are textbook examples of 4π electron antiaromatic five-membered ring systems. So far, they were reported only as short-lived intermediates generated under superacidic conditions or by flash photolysis. Attempts to prepare a m-terphenyl acylium cation by fluoride abstraction from a benzoyl fluoride gave rise to an isolable 9-hydroxy fluorenyl cation that formed by an intramolecular electrophilic attack at a flanking mesityl group prior to a 1,2-methyl shift and proton transfer to oxygen.

Carbocations are key intermediates in numerous organic reactions. Groundbreaking work by Olah in the 1970s demonstrated that many of these transient carbocations can be detected at low temperatures under superacidic conditions. However, most attempts to isolate these highly reactive species were impared by decomposition at the time.[1] With the introduction of new powerful Lewis acids and weakly coordinating anions, the situation gradually changed and in recent years the isolation and full characterization of many carbocations was achieved including a non-classical 2-norbornyl cation,[2] the benzenium ion,[3] hexahalobenzene radical cations,[4] the hexamethylbenzene dication[5] and cationic ring systems.[6]

Acylium ions play a significant role as intermediates in Friedel-Crafts reactions. In the solid state most acylium ions form ion pairs with their counterions.[7] This observation prompted us to attempt the synthesis of a kinetically-stabilized m-terphenylacylium cation by and confirmed by X-ray structure determination (Figure 1). The fluorenyl cation 2 is stable in chlorinated NMR solvents for a short period of time, but slowly degrades over the course of one day. In donor solvents (e.g. THF, Et2O) it turns immediately yellow. Even as a solid under inert conditions, it slowly degrades to become a yellow powder over the course of a few weeks at room temperature. Controlled deprotonation of 2 with NaOH afforded the related 9-fluorenone 3 as bright yellow crystals in quantitative yield (Scheme 1). The fluorenyl cation 2 is stable in chlorinated NMR solvents for a short period of time, but slowly degrades over the course of one day. In donor solvents (e.g. THF, Et2O) it turns immediately yellow. Even as a solid under inert conditions, it slowly degrades to become a yellow powder over the course of a few weeks at room temperature. Controlled deprotonation of 2 with NaOH afforded the related 9-fluorenone 3 as bright yellow crystals in quantitative yield. The identity of 1–3 was confirmed by the full assignment of the 1H and 13C NMR spectra and confirmed by X-ray structure determination (Figure 1).[13] In solution, 1 is characterized by its 19F NMR chemical shift (CDCl3) of δ = 52.2 ppm. It reveals a doublet in the 13C NMR spectrum for the ipso carbon atom at δ = 157.7 ppm with a coupling constant of J(13C–19F) = 357.2 Hz. Upon fluoride abstraction, the 13C spectrum (CD3Cl) of 2 shows a more strongly deshielded singlet at δ = 200.6 ppm for the ipso carbon atom. Furthermore, a new broad signal in the 1H NMR spectrum (CD3Cl) became

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Figure 1. Fluoride abstraction from 1 afforded the 9-hydroxy fluorenylium tetrachloroaluminate 2. Base hydrolysis of 2 gave the 9-fluorenone 3. Molecular structures of 1, 2 (counter ion omitted for clarity) and 3 showing 50% probability ellipsoids and the atom numbering scheme. Selected bond lengths [Å] of 1: C1-C2 1.406(3), C1-C16 1.496(3), C2-C7 1.406(3), C7-C8 1.418(3), C8-C16 1.444(3), O1-C16 1.287(2). Selected bond lengths [Å] of 3: C1-C2 1.406(3), C1-C16 1.496(3), C2-C7 1.484(3), C7-C8 1.414(3), C8-C16 1.501(3), O1-C16 1.209(3).

visible at δ = 9.71 ppm, which was assigned to the hydroxyl group in 9-position being involved in hydrogen bonding with the π-system of the mesityl ring. This value is significantly less deshielded than that observed for the parent 9-hydroxy fluorenylium ion (δ = 12.75 ppm), reported by Olah et al.12 According to their work, the relative deshielding of this proton is a measure for the charge density residing on the oxygen atom. Following along this argument, 2 possesses a rather low positive charge density there.13 In 3, the 13C NMR (CDCl3) resonance shows a nearly unchanged singlet at δ = 195.3 ppm. A UV/vis spectrum of 2 in CHCl3 (50 μM) shows a broad absorption maximum at λmax = 421 nm, which is also present in 3. In addition, 3 shows also two absorptions at λmax = 333 and 346 nm and shows a green-yellow luminescence with an excitation maximum of λmax = 320 nm and an emission maximum at λmax = 512 nm.

The molecular structures13 of 2 and 3 reveal the presence of fluorene scaffolds and indicate that a methyl group migration had taken place. In both five-membered ring structures, the C2-C7, C1-C16 and C8-C16 bond lengths are considerably longer than C1-C2 and C7-C8, which are shared with the anelated benzene rings. In the fluorenyl cation 2, the C–O bond length (1.287(2) Å) is significantly longer than in the fluorenone 3 (1.209(3) Å). Both values closely resemble those of protonated cyclopentanone (1.266(3) Å) and cyclopentanone (1.211(2) Å).13 In 2, the hydroxyl group points towards the π-electrons of the remaining mesityl group. In an effort to shed some light on the mechanism that led to the formation of 2, DFT calculations were carried out at the B3PW91/6-311+G* level of theory (Figure 2). The relative energy of the assumed initial product of the fluoride abstraction, namely the m-terphenylacylium ion, [2,6-MesC6H4CO]1+ (A) was arbitrarily set to zero. The acylium ion A undergoes an electrophilic attack at the ortho-position of one flanking mesityl group. The product of this attack, the arenium ion C is by 30 kJ mol⁻¹ energetically less favoured. Next, a 1,2-methyl shift takes place, which gave the arenium ion E, which is by 36.8 kJ mol⁻¹ energetically even less favoured than the acylium ion A. Only the last step is by −114 kJ mol⁻¹ energetically favoured. It entails a proton transfer from E to the fluorenyl cation G (the cation of 2). This last step involves the largest activation barrier, as the transition state F' is 154.2 kJ mol⁻¹ higher in energy than A. In a future study it should be taken into consideration if the proton transfer might as well be mediated by the [AlCl4]⁻ ion.

In order to qualitatively monitor the processes of bond formation and rapture along the proposed reaction coordinate, the Atoms-In-Molecules (AIM)16 and non-covalent interactions index (NCI)17 methods were applied to the DFT models A–G (Figure 3 and Figures S1–S3). The former provides a molecular graph exceeding the Lewis picture of chemical bonding, whereas the latter provides contact patches even for very weak interactions which not necessarily form a bond critical point (bcp) in AIM. The AIM graph of the transition state B' (electrophilic attack) closely resembles that of the intermediate C in that the CO-fragment is considerably bent and a C(O)···C ortho bcp is already formed despite the large C–C distance of 1.942 Å (Figure 3a). The O atom, now closer to the mesityl part on the opposite side, forms a weak O···H–C hydrogen bond, which is also visible in the NCI together with even weaker H···H contacts. In the transition state of the subsequent 1,2-methyl shift (D') the methyl C atom is still somewhat closer to the ortho-position (1.873 Å) than to the meta-position (1.880 Å). Accordingly, the AIM bond path, which approaches the Cortho···Cmeta bcp, bends away and finally connects the methyl C atom with the ortho C atom, resulting in a quasi T-shaped bonding scenario (Figure 3b). It might be stated, however, that D' is closer to the educt (intermediate C) than to the product (intermediate E). In the latter a second O···H–C hydrogen bond is then established. The energy demanding proton transfer (transition state F') shows that the proton in meta-position is still topologically connected to the mesityl ring despite a long C–H distance of 1.381 Å (Figure 3c). The out-of-plane bending (Cortho···Cmeta···Cmethyl angle; Cortho is the ortho C atom on the
opposite side of the mesityl ring) of the methyl group is reduced from 128° (intermediate C) to 152° (F#), which is half way to the value of 178° found in the final compound G. It is noted that the experimentally observed intramolecular hydrogen bridge is also present in the optimized structure of G, which suggests that it possesses a stabilizing effect to some extent. The NCI proves that non-covalent interactions are of minor importance for the reaction steps. Notably, transition states which are closer to the product are lower in energy than those which are closer to the starting compound in the current study.

The cyclopentadienyl cation as well as the central five-membered ring in the fluorenyl cation formally possess 4π electrons and according to the Hückel rule are antiaromatic, but it is still unclear what influence the two annelated aromatic benzene rings and the hydroxyl group in 9-position pose on the central five-membered ring. In an effort to address this question, we calculated nuclear-independent chemical shifts (NICS) for a number of aromatic and antiaromatic parents (Figure 4). The NICS(0) values of benzene and the cyclopentadienyl cation, determined at the ring critical points (rcp) are −8.08 and −13.14, whereas the NICS(1) values, referring to points perpendicular to the ring, 1 Å above the rcps are −10.21 and −10.45. Compared to these clearly aromatic benchmarks, the anti-aromatic cyclopentadienyl cation shows the largest deviation with NICS(0) and NICS(1) values of 88.96 and 67.45. Introduction of the hydroxyl group in 9-position dramatically reduces these values to 25.89 and 16.25. Going from the cyclopentadienyl cation to the fluorenyl cation has about the same effect as the values of the 5-membered ring decrease to 30.03 and 20.11. In turn, the NICS(0) and NICS(1) values of the two annelated aromatic benzene rings increase to 10.85 and 5.55 when compared to benzene. Both effects are accumulated in the 9-hydroxyfluorenyl cation with NICS(0) and NICS(1) values of 18.70 and 11.75 for the central five-membered ring. These values are very close to those calculated for G (Table S2). Thus, the two annelated aromatic benzene rings and the 9-hydroxy group outweigh the antiaromatic character, which provides a reasonable explanation as to why it was possible to isolate 2.

In summary, attempts to prepare a kinetically stabilized m-terphenyl acylium ion by fluoride abstraction from the benzoyl fluoride 1 gave the 9-hydroxy-1-mesityl-5,7,8-trimethyl fluorenyl cation 2 instead. The rearrangement was rationalized by an intramolecular electrophilic attack (Friedel Crafts reaction) of the initially formed m-terphenylacylium ion, [2,6-Mes$_2$C$_6$H$_3$CO]$^+$ at a flanking mesityl group, prior to a 1,2-methyl shift and a proton transfer to oxygen. This rearrangement is strongly reminiscent of the reaction between 2,6-(4-t-BuC$_6$H$_3$)$_2$C$_6$H$_3$Li with Cl$_2$BH·SMe$_2$, which gave 9-bora-fluorene rather than the expected bis(m-terphenyl)borane. It also resembles our previous attempts to prepare stable bis(m-terphenyl)-phosphonium ions by fluoride abstraction from (2,6-Mes$_2$C$_6$H$_3$)$_2$PF and [2,6-(Me$_5$C$_6$)$_2$C$_6$H$_3$)$_2$PF, which gave a (protonated) 9-phospha-fluorene and isomeric 9-phospha-fluorenium ions instead. The latter two reactions also involved...
methyl group migrations. The 9-hydroxy fluorenyl cation 2 comprises a central five-membered ring with formally 4π electrons, thus fulfilling the Hückel rule for antiaromaticity. The calculation of NICS values suggest that the antiaromatic character is compensated by the accumulative effect of the two annelated benzene rings and the hydroxyl group in 9-position.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** acylium ion · antiaromaticity · carbocation · electrophilic substitution · fluorenyl ion

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[13] Deposition Number 2063417 (for 1), 2063418 (for 2), and 2063419 (for 3) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.


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