1,3,5,7-Adamantanetetrakis(α,α-diphenylmethyl)tetrayl Tetracation: A Stable Tetrahedrally Arrayed Tetracation[1]

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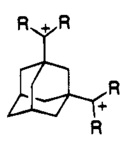
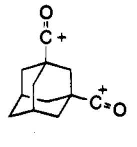
Received September 5, 1995

Recently we reported on the preparation and NMR spectroscopic study of a series of disubstituted adamantane-1,3-dimethyldiyl dications (**1**).[2] It was shown that these 1,5-distonic dications were stabilized both by their α,α-disubstitution and by favorable carbon−carbon bond homohyperconjugation involving the ideally aligned $\gamma-\delta$ bonds of the adamantyl framework. We are interested in systems of this type for the design and synthesis of stable molecular salts[3] with multiply charged adamantoid hydrocarbons suitable for the localization of positive charge at each of four tetrahedrally disposed charged groups or centers which can be used to construct self-assembled structures with suitable bidentate donors (see Figure 1). We report now a further step toward this goal, namely, the preparation and NMR spectroscopic characterization of a tetrahedrally arrayed tetracation based on the adamantane cage system. Tetracations themselves are exceptionally rare,[4] and long-lived tetracarbocations are presently unknown.



1a: R = Ph
1b: R = Me



1c

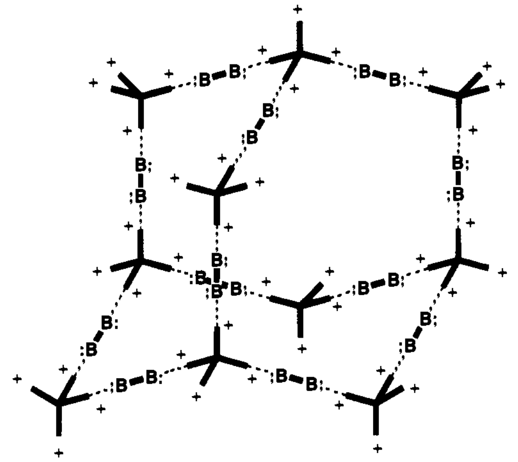
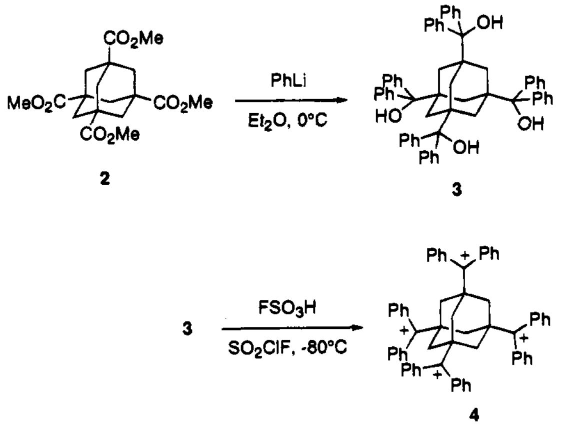


Figure 1. Schematic representation of a section of a hypothetical, self-assembling lattice of tetrahedrally arrayed tetracations and interposing bidentate Lewis bases.

Scheme 1



The precursor tetraol **3**[5a] was prepared in good yield (78%) by addition of excess phenyllithium (16 equiv) to an ether solution of the corresponding tetraester **2** at 0 °C (Scheme 1). The tetraester **2** itself is readily made via photochlorocarbonylation of adamantanecarboxylic acid.[6] Addition of fluorosulfuric acid to an SO_2ClF slurry of **3** at −80 °C gave upon vigorous stirring[7] an orange-colored solution, whose ^1H and ^{13}C NMR spectra are displayed as Figure 2. From this spectrum it is evident that the tetrahedral symmetry of the adamantane framework is preserved on ionization. On the basis of this evidence and the observed C^+ resonance at 233.5 ppm, typical for a diphenylalkyl carbenium cation,[8] the observed species is assigned to the tetracation **4**. The ^1H and ^{13}C chemical shifts for **4** in SO_2ClF at −50 °C were as follows: ^1H NMR δ 2.70 (s, 12H, CH_2), 7.05 (t, 16H, meta), 7.18 (d, 16H, ortho), 7.70 (t, 8H, para); ^{13}C NMR δ 233.5 (C^+), 148.0 (para), 142.1 (ipso), 140.7 (ortho), 130.4 (meta), 52.5 (C), 44.7 (CH_2). The assignments have been made on the basis of the multiplicities observed in the ^1H-coupled ^{13}C NMR spectrum and by comparison with other known benzylic carbocations.[8] The tetracation (**4**) was stable from −80 to −40 °C, through which range no temperature-dependent changes were observed. Above −40 °C slow decomposition began to take place (indicated by new signals in the ^{13}C NMR).

Comparison of the ^{13}C NMR data for **4** and its disubstituted analog (**1a**)[2] is quite informative concerning the consequences of introducing two additional cationic charges into the system. Although ^{13}C NMR chemical shifts cannot be quantitatively correlated to charge densities, there is considerable evidence[9] indicating that the chemical shifts for carbon atoms of similar hybridization and substitution in hydrocarbon molecules significantly reflect electron densities. Interestingly, although **4**

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(5) (a) NMR data for **3**: ^1H NMR ($CDCl_3$) δ 1.67 (s, 12H), 7.10−7.18 (m, 20H), 7.24−7.30 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 36.0, 43.2, 82.6, 126.5, 127.1, 128.5, 145.0. (b) NMR data for 1,3,5,7-tetrakis(diphenylhydroxymethyl)cubane: ^1H NMR ($CDCl_3$) δ 4.38 (s, 4H), 7.18 (s, 40H); ^{13}C NMR ($CDCl_3$) δ 50.6, 53.8, 77.7, 126.8, 127.2, 128.1, 143.8.

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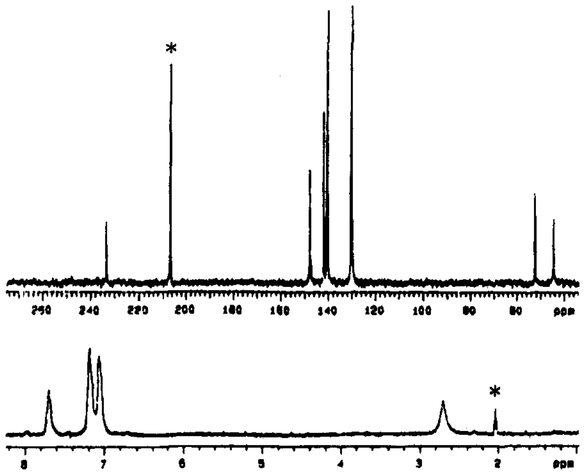

Figure 2. ^{13}C (upper) and ^{1}H (lower) NMR spectra of the 1,3,5,7-adamantanetetrakis(α,α-diphenylmethyl)tetrayl tetracation (**4**). In SO_2ClF at −50 °C. Peaks with asterisks; acetone-d$_6$. Chemical shifts in ppm relative to external acetone-d_6 (^{13}C NMR, CD_3 = 29.8 ppm; ^{1}H NMR, CHD_2 = 2.04 ppm).

bears two additional charges, the chemical shifts of the adamantyl bridgehead carbons and of the formal cationic sites are actually shielded relative to **1a** by 13.1 ppm for each C^+ and by 2.9 ppm for each bridgehead site relative to those in **1a**. However, each carbon of the phenyl groups in **4** is more deshielded than those in **1a**. In fact the total deshielding of two phenyl groups in **4**, 12.6 ppm, very nearly accounts for the shielding of the formal cationic centers. It would appear, on the basis of these observations, that in order to offset the additional charge−charge repulsion in **4**, relative to **1a**, greater delocalization of positive charge into the phenyl groups is effected. The additional deshieding experienced by the phenyl groups of **4** is also greatest for the ortho and para carbons, as would be expected on the grounds of the usual resonance contributors.[8] The small shielding of the bridgehead carbons in **4** relative to **1a** may reflect that additional homohyperconjugation also stabilizes **4**. While the tetrahedrally symmetric cubane-based analog of **3**^{5b} was prepared in 73% yield from the corresponding tetramethyl ester,[10] it did not afford the corresponding tetracation as a stable species on ionization with FSO_3H/SO_2ClF. This is consistent with our previous observations[11] and those of others[12] that cubylcarbinyl cations, even bearing strongly electron donating groups, are extremely prone to Wagner−Meerwein rearrangements due to the ring strain of the cubyl framework.

In conclusion, we have succeeded in preparing and characterizing the first stable tetrahedrally arrayed tetracation. Similar polycarbocationic systems could play a significant role in materials science[3] or cationically initiated dendridic polymerizations.[13,14] We are now continuing our work in these areas.

Acknowledgment. Partial support of our work by the National Science Foundation is gratefully acknowledged.

JA9530580

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