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Preparation and ^{13}C NMR Spectroscopic Study of Disubstituted Adamantane-1,3-dimethyldiyl Dications[1a]

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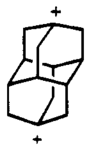
A series of substituted adamantane-1,3-dimethyldiyl dications **5** has been prepared by the ionization of α,α,α′,α′-tetrasubstituted-1,3-adamantanedimethyl diols **6** in superacidic media. The dications were stable with groups such as phenyl and methyl, however, unstable with cyclopropyl groups. The ^{13}C NMR spectroscopic study of the obtained dications clearly indicates that the positive charges are more delocalized into the substituents due to the close proximity of the cationic centers through the adamantyl cage. These studies are informative in probing cage compounds with multiply-charged centers.

Introduction

Studies on carbodications[1b] are more limited in comparison to those on carbomonocations. Previous studies on carbodications have shown that dipositive ions can in general be generated if the carbocation centers are separated by at least two carbon atoms from each other.[2] The charge−charge repulsion leads to increasing destabilization of the dication when the charged centers are brought within closer proximity. Adamandoid 1,6-dications such as the diamantane-4,9-diyl dication **1** and 1,1′-bisadamantane-3,3′-diyl dication **2** have been succesfully prepared and show similar NMR spectral characteristics as the monopositive adamantyl cations.[3] While attempts to form dipositive centers at the 1,4-position (i.e. two carbon separation) of a single adamantyl skeleton were unsuccessful, generation of two cationic centers into a single adamantanoid skeleton has been shown to be stable when the charge is separated by at least three carbons and additional stabilization is provided via electron-donating groups such as phenyl or cyclopropyl.[4]



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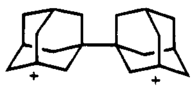

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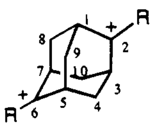

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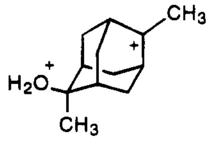

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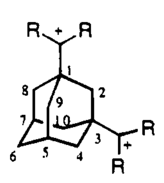
R = CH_3, C_6H_5, $c\text{-}C_3H_5$

Such 1,5-carbodication systems have been successfully prepared and studied by NMR spectroscopy on the 2,6-disubstituted 2,6-adamantanediyl dications **3**-R. Attempted preparation of secondary 2,6-adamantanediyl dication by the ionization of the secondary 2,6-diol under a variety of conditions led only to diprotonated diol. Furthermore, ionization of the dimethyl diol, however, gave only the monocation-monooxonium ion **4** which indicates that the methyl groups are also ineffective in stabilizing the dicationic species.[4]

Similar charge stabilization is expected via a three-carbon separation arrangement in an α,α-disubstituted 1,3-adamantanedimethyldiyl system **5**-R (*vide infra*). Such bridgehead-substituted structures introduce two cationic charged centers adjacent to the adamantanoid skeleton in comparison to **3**. Enhanced stabilization in **5**-R is anticipated due to tetrasubstituted nature as well as adjacent bridgehead hyperconjugative stabilization of the dicationic centers relative to the 2,6-disubstituted adamantyl systems.



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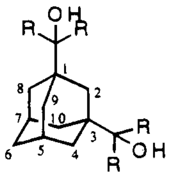

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Our interest in investigating these systems lies in the eventual design and development of stable molecular salts[5,6] with multiply charged adamantanoid hydrocarbons suitable for the localization of positive charge at each of four tetrahedrally disposed charged groups or centers. We now report the preparation and NMR spectroscopic investigation of α,α-disubstituted 1,3-adamantanedimethyldiyl dications, **5**-R.

[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1995.

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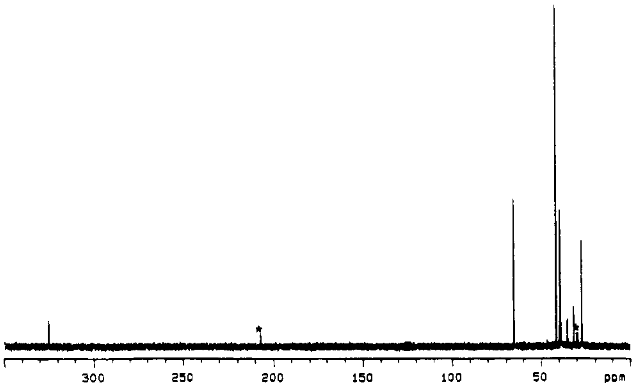


Figure 1. 75.4 MHz Proton-decoupled ^{13}C NMR spectrum of **5**-CH_3 in SbF_5/SO_2ClF at −80 °C. * denotes signals due to acetone-d_6.

Results and Discussion

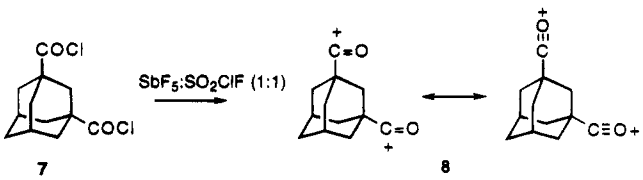
The tetrasubstituted alcohols **6**-R were prepared starting from commercially available dimethyl-1,3-adamantanedicarboxylate (see Experimental Section). The diacid chloride **7** was prepared from the corresponding dicarboxylic acid.

Ionization of the tetramethyl diol **6**-CH_3 in SbF_5:SO_2ClF (1:1) at −80 °C provided the 1,3-adamantane bis(α,α-dimethylmethyldiyl) dication **5**-CH_3 as indicated by the ^{13}C resonance at 324 ppm (Figure 1). The chemical shifts of dicationic carbons in **5**-CH_3 (Table 1) are comparable to the (C_2) resonance observed for the monocation-monooxonium **4**.[4] Both systems provide a three-carbon separation between ionic centers; however, the additional stabilization afforded in the 1,3-adamantyl arrangement allows complete ionization of the second carbon to occur. Further, we attribute the improved stability of the 1,3-adamantane bis(α,α-dimethylmethyldiyl) dication over the 2,6-disubstituted system to the extended tertiary hyperconjugation of the bridgehead carbons as well as the hyperconjugative stabilization of the methyl groups. Of particular interest in this system are the tertiary (C_5, C_7) carbons which show slightly shielded resonances at δ ^{13}C 26.4 in comparison to the corresponding neutral diol **6**-CH_3 which appear at δ ^{13}C 28.8. This increased shielding indicates the presence of reverse polarization effects[7] throughout the 1,3-adamantane tetrasubstituted framework. This is also supported by the fact that the resonances of neighboring carbons (C_4, C_8, C_9, C_{10}) in **5**-CH_3 at δ ^{13}C 39.8 are deshielded in comparison with the corresponding carbons in **6**-CH_3 which appear at δ ^{13}C 35.7. However, the remaining skeletal carbons throughout the adamantyl framework show comparable deshielding to the monocation-monooxonium ion of **4**.

Ionization of 1,3-adamantane bis(α,α-diphenylmethyl) diol **6**-C_6H_5 in 1:1 SbF_5:FSO_3H/SO_2ClF cleanly gave the 1,3-adamantane bis(α,α-diphenylmethydiyl) dication **5**-C_6H_5 as indicated by the presence of ten ^{13}C resonances in its proton decoupled ^{13}C NMR spectrum (Table 1). The cationic carbons resonate at δ ^{13}C 245.6 which is markedly shielded compared to the C_2 carbon of cation in **3**-C_6H_5 at δ ^{13}C 252.3.[4] The *ipso* and *para* carbons of the four phenyl groups remain relatively unaffected at δ ^{13}C 141.7 and δ ^{13}C 144.8, respectively, when compared to the *para* carbons of phenyl groups in **3**-C_6H_5 at δ ^{13}C 160.1. Furthermore, the C_1 and C_3 carbons of **5**-C_6H_5 at the adamantyl bridgehead positions resonate at δ ^{13}C 55.4 indicating some amount of charge dispersal into the adjacent adamantane cage. The other cage carbons show relatively less than expected deshielding. Of course in the presently observed 1,3-diyl dication **5**-C_6H_5, each positive charge is delocalized into two phenyl groups resulting in benzhydril-type delocalization. On the other hand, in **3**-C_6H_5 each positive charge is delocalized into one phenyl group resulting in benzylic-type delocalization.

Ground state geometries of the dication were optimized using tripos force field at MNDO and AM1 levels.[8] The dihedral angles along the plane of the phenyl-carbocation center show one of the phenyl groups nearly planar to the carbocation center at 175.8° with the adjacent phenyl closer to the orthoganol at 74.4°. The minimized geometry indicates the effects of a sterically congested arrangement with a high barrier of rotation required for both phenyl groups to assume coplanarity. The average of the charge delocalization between these two electron-donating phenyl groups is also reflected in their *para* carbon chemical shifts.

We have also studied the ionization of 1,3-adamantane bis(α,α-dicyclopropylmethyl) diol (**6**-c-C_3H_5) under a variety of acidic conditions. In FSO_3H/SO_2ClF, SbF_5/SO_2ClF, or SbF_5:FSO_3H/SO_2ClF at −78 °C the tetracyclopropyl diol decomposed and no discernible spectra could be obtained. However in SbF_5:FSO_3H/SO_2 solution the alcohol gave an orange colored solution whose ^{13}C NMR spectrum at −65 °C indicated the following absorptions: δ ^{13}C 275.3 (s), 81.7 (d, J = 174.0 Hz), 63.7 (d, J = 183.2 Hz), 55.8 (t, J = 172.2 Hz), 40.3 (t, J = 123.6 Hz), 39.1 (s), 38.9 (t, J = 123.6 Hz), 37.9 (t, J = 123.4), 33.8 (d, J = 134.4 Hz), 27.9 (t, J = 136.4 Hz), 22.7 (t, J = 136.4 Hz), 21.5 (t, J = 136.0 Hz). The data indicates a clear carbocationic center at δ ^{13}C 275.3, but the large number of peaks (total 13) observed excludes the formation of the symmetrical 1,3-adamantane bis(α,α-dicyclopropylmethyldiyl) dication **5**-c-C_3H_5. However, the exact structure of the species in solution is difficult to assign based on NMR data alone. Our attempts to quench the species to a discernible compound were unsuccessful.



Dissolution of the diacyl chloride **7** in 1:1 SbF_5/SO_2ClF at −80 °C gave the corresponding 1,3-adamantanedicarbonyl dication **8**. The ^{13}C NMR chemical shift of the carbonyl carbons at δ ^{13}C 147.5 reveals that the positive charges in **8** reside mostly on the oxygen atoms, with increased shielding contribution from the acylium resonance structure when compared to that in parent carbonyl chloride (δ ^{13}C 178.0). The acylium resonance structure approximates the strong magnetic anisotropies of sp hybridized bonds.[9] Comparison of the ^{13}C chemical shifts of neutral precursor (see Experimental Section for

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(8) Calculations were performed with the Spartan program on an IBM RS/6000 Model 560 computer.

Table 1. ^{13}C NMR Chemical Shifts[a] of the Adamantane 1,3-Disubstituted Dimethyldiyl Dications 5-R

ion	C^+	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	other
5-CH_3	324.1	65.4	35.5	65.4	39.6	27.4	31.9	27.4	39.6	39.6	39.6	CH_3, 42.1
5-C_6H_5	245.6	55.4	44.8	55.4	43.4	28.7	32.4	28.7	43.8	43.8	43.8	C_{ipso}, 141.7; C_o, 139.3; C_m, 129.1; C_p, 144.8
8		46.6	32.7	32.9	23.3	29.2	30.6	29.2	23.3	23.3	23.3	CO, 147.5

[a] All chemical shifts are in ppm (±0.1) in 1:1 FSO_3H:SbF_5/SO_2ClF at −80 °C unless otherwise stated and are referenced to external acetone-d_6 capillary.

the data) to the dication indicates a shielding region of the electron circulation induced by the magnetic fields. Thus, in all the adamantyl carbons with the exception of C_1 and C_3 bridgeheads we observe a shift to higher field strength. The observed chemical shift data for dication **8** are explained on this basis.

Olah, Schleyer, and their co-workers introduced a simple criterion for distinguishing classical carbocations from bridged species, using ^{13}C NMR chemical shift additivity.[10] The summation of ^{13}C NMR chemical shifts of classical carbocations, as compared with those of their corresponding neutral hydrocarbons, are typically very large, and their chemical shifts additivities differ by about 350 ppm (or more). Difference in the summation of the chemical shifts for nonclassical carbocations is significantly smaller, usually less than 200 ppm. This method has been applied to the dication **5**-CH_3. Since the parent hydrocarbon of the diol **6**-CH_3 is not known, we have estimated its additive chemical shift value as 507.8 ppm by subtracting 100 ppm from the sum of carbon chemical shifts of **6**-CH_3 (the value of 100 ppm being the usual chemical shift difference of ditertiary carbinols and their hydrocarbon analogs[11]). The additive ^{13}C chemical shift for the dication **5**-CH_3 at −80 °C is 1228 ppm. The summation difference of these chemical shifts ($\Delta\ \Sigma\delta$) corresponds to 720.2 ppm, i.e. 360 ppm per unit positive charge, which is commensurate to the values typical of classical monocarbocation. Thus the dication **5**-CH_3 is "classical" in that their point charges are substantially localized and not distributed throughout the adamantyl cage network. Such a result may be favorable in designing a multiply charged system with four tetrahedrally disposed point charges.

Conclusion

In conclusion, we have successfully prepared and characterized by ^{13}C NMR spectroscopy a series of substituted adamantane-1,3-dimethyldiyl dications. Such dications are stable even when the tertiary dication centers are substituted with methyl groups. The unique stabilization afforded via the tetrasubstitution as well as bridgehead hyperconjugation encourages one to carry out further investigations into multiply charged systems with similar three-carbon separation arrangements.

Experimental Section

Diethyl ether was distilled from sodium−benzophenone ketyl immediately before use. Lithium metal dispersion in mineral oil was obtained from Aldrich and used as received. Dimethyl-1,3-adamantanedicarboxylate and 1,3-adamantanedicarboxylic acid were purchased from Aldrich. Mass spectra were carried out on a Finnigan-Mat/Incos-50 mass spectrometer, using DEP probe at 70 eV. Melting points (uncorrected) were determined using a Mettler FP1 melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a 200 or a 300 MHz equipped with a variable temperature probe. The ^{1}H and ^{13}C NMR chemical shifts for the carbocations were referenced with respect to the external capillary acetone-d_6.

1,3-Adamantane Bis(α,α-diphenylmethyl) Diol (6-C_6H_5). Under an argon atmosphere in flame-dried glassware, a solution of bromobenzene (5 mL, 47 mmol) and (0.255 g, 1.1 mmol) dimethyl 1,3-adamantanedicarboxylate in diethyl ether (5 mL) was added dropwise at 0 °C with vigorous stirring to a mixture of lithium dispersion (1 mL) in 10 mL of diethyl ether over a 5 min period. Following overnight stirring at room temperature, the excess lithium was destroyed by careful addition of saturated aqueous ammonium chloride solution and the mixture was extracted with ether. The ether extract was then washed with concd brine, dried (Na_2SO_4), and concentrated *in vacuo*. Recrystallization from pure ethanol gave pure diol: 0.338 g (68%); mp 213 °C; IR (KBr) ν 3621, 3466, 2979, 2865, 1489, 1319, 1014, 788, 755 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.49, 7.46, 7.23, 7.20, 2.23, 2.05, 1.73, 1.32, 1.26. ^{13}C NMR (50 MHz, $CDCl_3$) δ 145.3, 128.6, 127.2, 126.5, 82.4, 42.08, 36.9, 36.7, 36.3, 29.1. Anal. Calcd for $C_{36}H_{36}O_2$: C, 86.36; H, 7.25. Found: C, 86.13; H, 7.56.

1,3-Adamantane Bis(α,α-dimethylmethyl) Diol (6-CH_3). A solution of 3.0 M methylmagnesium bromide (7 mL, 21 mmol) was added dropwise at 0 °C to (0.300 g, 1.2 mmol) dimethyl 1,3-adamantanedicarboxylate in ether (10 mL) with vigorous stirring. Following overnight stirring at room temperature, the excess Grignard was destroyed by careful addition of saturated aqueous ammonium chloride solution, and the mixture was extracted with ether. The ether extract was then washed with concd brine, dried (Na_2SO_4), and concentrated *in vacuo*. Recrystallization from ethanol gave pure alcohol 0.250 g (83%): mp 168.0 °C; IR (KBr) ν 3475, 2995, 2818, 1444, 1379, 1211, 1154, 944 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.1, 1.6, 1.5, 1.4, 1.16 ^{13}C NMR (50 MHz, $CDCl_3$) δ 74.8, 39.5, 36.5, 35.7, 34.6, 28.8, 24.4. Anal. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 76.18; H, 11.55.

1,3-Adamantane Bis(α,α-dicyclopropylmethyl) Diol (6-c-C_3H_5). Under an argon atmosphere in flame-dried glassware, a solution of cyclopropyl bromide (3 mL, 37.8 mmol) and (0.300 g, 1.2 mmol) dimethyl 1,3-adamantanedicarboxylate in ether (10 mL) was added dropwise at 0 °C with vigorous stirring to a mixture of lithium dispersion (21 mmol, 3.3% Na) in ether over a 5 min period. The temperature was maintained at constant ice-bath temperature for 0.5 h and then stirred at rt overnight. The excess lithium was destroyed by careful addition of saturated aqueous ammonium chloride solution. The mixture was extracted with ether. The ether extract was then washed with concd brine, dried (Na_2SO_4), and concentrated *in vacuo*. Recrystallization from ethanol yielded 0.254 g (60%) of the alcohol: mp 124 °C; IR (KBr) ν 3528, 3004, 2859, 1311, 1292, 1185, 1033, 962, 850 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.2, 1.9−1.7, 1.6, 1.58, m (1.0−0.8), m (0.5−0.2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 73.4, 42.6, 36.9, 36.6, 36.5, 28.8, 14.3, 0.6, 0.4. Anal. Calcd for $C_{24}H_{36}O_2$: C, 80.86; H, 10.18. Found: C, 81.09; H, 10.30.

1,3-Adamantanedicarbonyl Chloride (7). Under a nitrogen atmosphere in a flame-dried, three-necked flask fitted with a reflux condenser connected at the top to a gas absorption trap was added 1,3-adamantanedicarboxylic acid (1 g, 4.5 mmol) to (10 mL, 0.13 mol) freshly distilled thionyl chloride. The mixture was refluxed with vigorous stirring for 2 h and

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the excess thionyl chloride distilled off. The mixture was cooled to rt and 5 mL distilled benzene was added to the remaining oil which was further distilled until a white precipitate appeared. The product was placed under vacuum for 4 h and the remaining white solid (crude product 1.1 g, 94% yield) collected under nitrogen: mp 94 °C; IR (KBr) ν 2917, 2864, 1778, 1456, 1274, 1062, 830, cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.8, m (1.5−1.47), 1.43, 1.35, 1.3; ^{13}C NMR (75 MHz, CDCl$_3$) δ 178.0, 51.1, 39.6, 37.4, 34.2, 27.6.

Preparation of Carbocations. FSO$_3$H and SbF$_5$ were freshly distilled before use. A 1:1 mixture of FSO$_3$H or SbF$_5$/FSO$_3$H and SO$_2$ClF was added to a suspension of the precursor alcohols in SO$_2$ClF contained in 5-mm NMR tubes at 78 °C in dry ice/acetone bath. Efficient mixing of the solution was effected using a vortex stirrer.

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