

Preparation, ^{13}C NMR/DFT/IGLO Study of Benzylic Mono- and Dications, and Attempted Preparation of a Trication¹

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Abstract: Substituted benzylic mono- and dications were prepared and investigated by ^1H and ^{13}C NMR spectroscopy and DFT/IGLO calculations. Combined experimental and theoretical study suggest that the structure **1a** is the major resonance contributor to the 2,4,6-trimethylbenzyl cation **1**. Similar results were also found for the 2,4,6-dimethyl-4-*tert*-butylbenzyl **2** and 2,3,4,5,6-pentamethylbenzyl cation **3**. It was found that the structure **4a** is the predominant resonance contributor to the overall structure of 2,6-dimethylmesityldiyl dication **4** wherein the dienylyl and allylic cation units are insulated from each other. Similar studies indicate structure **5a** as the predominant canonical structure for 5-methoxy-2,6-dimethyl-*m*-xylyldiyl dication **5** wherein the dienylyl and oxoallylic cation units are insulated from each other. Attempts to generate the 2,3,5,6-tetramethyl-1,4-dimethylbenzenediyl dication **8** was, however, not successful as were the generation of the 2,4,6-trimethylmesityltriyl trication **10** by ionization of 2,4,6-bis(chloromethyl)-mesitylene. The resulting ion was characterized as a chloromethyl substituted dication **9**.

Introduction

The study of long-lived aliphatic and aromatic carbocations and carbodications is of considerable interest.^{2–4} A number of ring-substituted primary benzylic monocations (aryl carbenium ions) were observed as long-lived ions by Olah et al.⁵ in 1966 and were characterized by ^1H NMR spectroscopy. No long-lived phenyl-1,3-dimethyldiyl dication wherein the carbocation centers are both primary, however, has been reported. Previous studies on carbodications have shown that in the absence of aryl stabilization of the carbocation centers, long-lived dipositive ions can be generated only if the carbocationic centers are separated by at least two carbon atoms and the carbenium centers are tertiary.⁶ We reported successful characterization of 2,10-*para*-[3².5⁶]octahedranedimethyl dication a novel bicyclicpropylmethyl dication.⁷ Recently we also reported in a preliminary communication¹ the preparation and NMR/DFT/IGLO study of the 2,6-dimethylmesityldiyl dication. The dication can also be considered a substituted benzene dication, a unique dienylyl and allylic dication system.

We now wish to report the preparation, ^{13}C NMR spectroscopic characterization, and DFT/IGLO study of several benzylic monocations and dications. These include the preparation and study of dienylyl-allylic 2,6-dimethylmesityldiyl dication and dienylyl-oxoallylic 3-methoxy-2,6-dimethyl-*m*-xylyldiyl dication and comparison of their structure with that of the bisallyl benzene dication. The study also includes comparison of calculated data with experimentally observed results. No such comparisons have so far been reported for benzylic cations. We also report attempted preparation of the 2,4,6-trimethylmesityltriyl trication.

Results and Discussion

The benzylic mono and dications were prepared in superacid solutions at $-78\text{ }^\circ\text{C}$ by the ionization of their respective halides under previously established conditions and studied by ^1H and ^{13}C NMR spectroscopy. The structures of the benzyl monocation and dications were fully optimized at the DFT⁸ B3LYP/3-21G level using the GAUSSIAN-94⁹ package of programs. ^{13}C NMR chemical shifts were calculated by IGLO methods¹⁰ using B3LYP/3-21G geometries (i.e., at the IGLO/DZ//B3LYP/3-21G level). Benzylic dications were further optimized at the higher B3LYP/6-31G* level, and the ^{13}C NMR chemical shifts were calculated at the IGLO/DZ using B3LYP/6-31G* geometries (i.e., IGLO/DZ//B3LYP/6-31G* level). Löwdin bond orders¹¹ and natural bond orbital (NBO)¹² σ charges were calculated at the B3LYP/6-31G*//B3LYP/6-31G* level.

Benzylic Monocations 1–3. Benzylic monocations 1–3 were obtained by dissolving the corresponding benzyl chlorides

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(1) Stable Carbocations Part 303. For Part 302, see: Olah, G. A.; Shamma, T.; Burcher, A.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1997**, *119*, 3407.

(2) For major reviews, see: (a) Olah, G. A.; Pittman, C. U., Jr.; Symons, M. C. R. *Carbocation Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Interscience: New York, NY, 1968; Vol. 1. (b) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173. (c) Olah, G. A. *Acc. Chem. Res.* **1976**, *9*, 410. (d) Olah, G. A. *Top. Curr. Chem.* **1979**, *80*, 21.

(3) Olah, G. A. *Chem. Scr.* **1981**, *18*, 97.

(4) Prakash, G. K. S.; Rawdah, T.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 390.

(5) (a) Cupas, C. A.; Comisarow, M. B.; Olah, G. A. *J. Am. Chem. Soc.* **1966**, *88*, 361. (b) Bollinger, J. M.; Comisarow, M. B.; Cupas, C. A.; Olah, G. A. *J. Am. Chem. Soc.* **1967**, *89*, 5687. (c) Olah, G. A.; Porter, R. D.; Jeuell, C. L.; White, A. M. *J. Am. Chem. Soc.* **1972**, *94*, 2044.

(6) (a) Olah, G. A.; Grant, J. L.; Spear, R. J.; Bollinger, J. M.; Serianz, A.; Sipos, G. *J. Am. Chem. Soc.* **1976**, *98*, 250. (b) Olah, G. A.; Cupas, C. A.; Friday, K. J.; Bollinger, J. M.; Woolfe, M. L. *J. Am. Chem. Soc.* **1967**, *89*, 156. (c) Olah, G. A.; Reddy, V. P.; Lee, G.; Casanova, J.; Prakash, G. K. S. *J. Org. Chem.* **1993**, *58*, 1639. (d) Olah, G. A.; Hartz, N.; Rasul, G.; Prakash, G. K. S.; Burkhart, M.; Lammertsma, K. *J. Am. Chem. Soc.* **1994**, *116*, 3187.

(7) Olah, G. A.; Buchhiz, B.; Prakash, G. K. S.; Rasul, G.; Sosnowski, J. J.; Murray Jr. R. K.; Kusenetsov, M. A.; Liang, S.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 13.

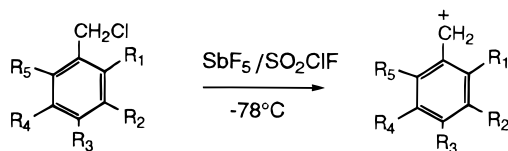
(8) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

(9) Gaussian 94 (Revision A.1); Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

(10) (a) Schindler, M. *J. Am. Chem. Soc.* **1987**, *109*, 1020. (b) Kutzelnigg, W.; Fleischer, U.; Schindler, M. *NMR Basic Princ. Prog.* **1991**, *23*, 165.

(11) Löwdin, P. O. *Phys. Rev.* **1955**, *97*, 1474.

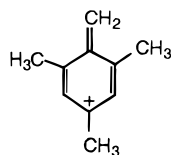
Scheme 1



- 1 $R_1 = \text{CH}_3$, $R_2 = \text{H}$, $R_3 = \text{CH}_3$, $R_4 = \text{H}$, and $R_5 = \text{CH}_3$
- 2 $R_1 = \text{CH}_3$, $R_2 = \text{H}$, $R_3 = t\text{-butyl}$, $R_4 = \text{H}$, and $R_5 = \text{CH}_3$
- 3 $R_1 = \text{CH}_3$, $R_2 = \text{CH}_3$, $R_3 = \text{CH}_3$, $R_4 = \text{CH}_3$, and $R_5 = \text{CH}_3$

in excess of $\text{SbF}_5\text{-SO}_2\text{ClF}$ solutions at -78°C (Scheme 1). All ions were stable at -78°C , and the ^{13}C NMR spectra of the solutions of these ions were well resolved. Previously the cations **1–3** were characterized by only ^1H NMR spectroscopy.⁴ Presently obtained ^{13}C NMR data of the cations are given in Table 1.

The 75 MHz ^{13}C NMR spectrum of the 2,4,6-trimethylbenzyl cation **1** exhibited seven peaks. The peak at $\delta^{13}\text{C}$ 169.5 (triplet in the proton coupled ^{13}C NMR spectrum) is due to the positively charged benzylic carbon C_1 . The most deshielded peak in the spectrum at $\delta^{13}\text{C}$ 188.5 is assigned to the C_5 carbon, which is 19.0 ppm more deshielded than that of benzylic carbon C_1 . This suggests that the resonance structure **1a** makes an important contribution to the overall stabilization of the ion **1**.

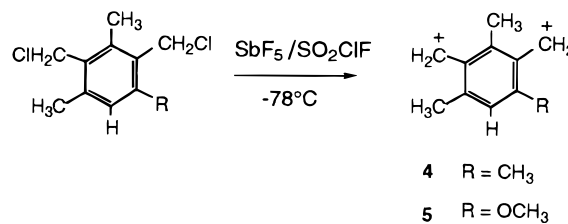
**1a**

This is also in agreement with the calculated structure of **1** (Figure 1). The $\text{C}_1\text{-C}_2$ (1.361 Å) and $\text{C}_3\text{-C}_4$ (1.375 Å) bond distances are close to that of a double bond, but the $\text{C}_2\text{-C}_7$ (1.471 Å) and $\text{C}_4\text{-C}_5$ (1.416 Å) bond distances are significantly longer than a double bond. Similarly the 2,6-dimethyl-4-*tert*-butylbenzyl cation **2** was also prepared from its precursor 2,6-dimethyl-4-*tert*-butylbenzyl chloride. The resonance due to benzylic carbon C_1 of **2** at $\delta^{13}\text{C}$ 170.1 is only 0.6 ppm more deshielded than that of **1**. However, the C_5 peak of **2** at $\delta^{13}\text{C}$ 198.4 is 9.9 ppm more deshielded than that of **1** due to *tert*-butyl substitution. The calculated structure of **2** is given in Figure 1. $\delta^{13}\text{C}$ of C_1 and C_5 in the ^{13}C NMR spectrum of 2,3,4,5,6-pentamethylbenzyl cation **3** is similar to those of **1**. Calculated structure of **3** is also very similar to the calculated structure of **1**. IGLO calculated ^{13}C NMR chemical shifts of cations **1–3** correlate well with the experimentally obtained data (Table 1). The calculated ^{13}C NMR chemical shifts of carbocationic centers (CH_2 carbon) are 10.6–12.5 ppm more deshielded than the experimentally observed results. The agreement between experimental and calculated values may be improved by using correlated level calculations such as GIAO-MP2 method.^{12b} However, GIAO-MP2 calculations using ACES II program^{12c} are presently limited to only small size molecules.

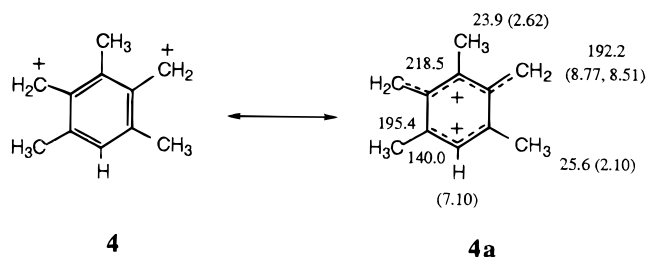
(12) (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.; Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Gauss, J. *J. Chem. Phys. Lett.* **1992**, *191*, 614. Gauss, J. *J. Chem. Phys.* **1993**, *99*, 3629. (c) ACES II, an ab initio program system by Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J.; Quantum Theory Project, University of Florida, 1991 and 1992.

Dibenzylidyl Dications 4 and 5. 2,6-Dimethylmesityldiyl dication **4** and 2,6-dimethyl-5-methoxy-*m*-xylyldiyl dication **5** were prepared by the ionization of their precursors 2,6-bis(chloromethyl)mesitylene and 2,4-bis(chloromethyl)-3,5-dimethylanisole, respectively, in 5-fold excess of SbF_5 in $\text{SO}_2\text{-ClF}$ at -78°C (Scheme 2).

Scheme 2

**4** $R = \text{CH}_3$ **5** $R = \text{OCH}_3$

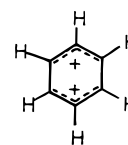
Scheme 3

**4****4a**

The 75 MHz ^{13}C NMR spectrum of the ion **4** shows seven well-resolved peaks at $\delta^{13}\text{C}$ 218.5 (s), 198.2 (t, $J_{\text{C,H}} = 170.3$ Hz) 195.4 (s), 143.9 (s), 140.0 (d, $J_{\text{C,H}} = 177.3$ Hz), 25.6 (q, $J_{\text{C,H}} = 131.9$ Hz), 23.9 (q, $J_{\text{C,H}} = 132.3$ Hz). The 300-MHz ^1H NMR showed absorptions at $\delta^1\text{H}$ 8.77 (br, 2H), 8.51 (br, 2H), 7.10 (singlet, 1H), 2.62 (singlet, 3H), and 2.10 (singlet, 6H). Based on the observed NMR data the dienylc allylic dication structure **4a** appears to be the predominant resonance contributor to the overall structure **4**. The ion is remarkably stable even at -10°C .

The ^1H (in brackets) and ^{13}C NMR chemical shift assignments are also shown on the structure **4a** in Scheme 3. The unusual stability of the dication can be attributed to the two isolated, highly stabilized dienylc and allylic cationic fragments in the structure **4a**.

The structure **4a** resembles the bisallylic benzene dication **6**. The benzene dication **6** is experimentally still unknown but di- and polycyclic benzoanalogs were obtained by two-electron oxidation of the corresponding arenes by SbF_5 .¹³ MINDO/3 calculations by Dewar and co-workers¹⁴ showed that the benzene dication **6** favors a C_{2h} chair conformation as the most stable form, with essentially isolated allyl cation units. Subsequently Schleyer et al. showed¹⁵ that **6** is subject to Jahn-Teller distortion forming a double-allyl dication.

**6**

(13) Olah, G. A.; Forsyth, D.; *J. Am. Chem. Soc.* **1976**, *98*, 4086. Olah, G. A.; Sing, B. P.; *J. Org. Chem.* **1983**, *48*, 4830.

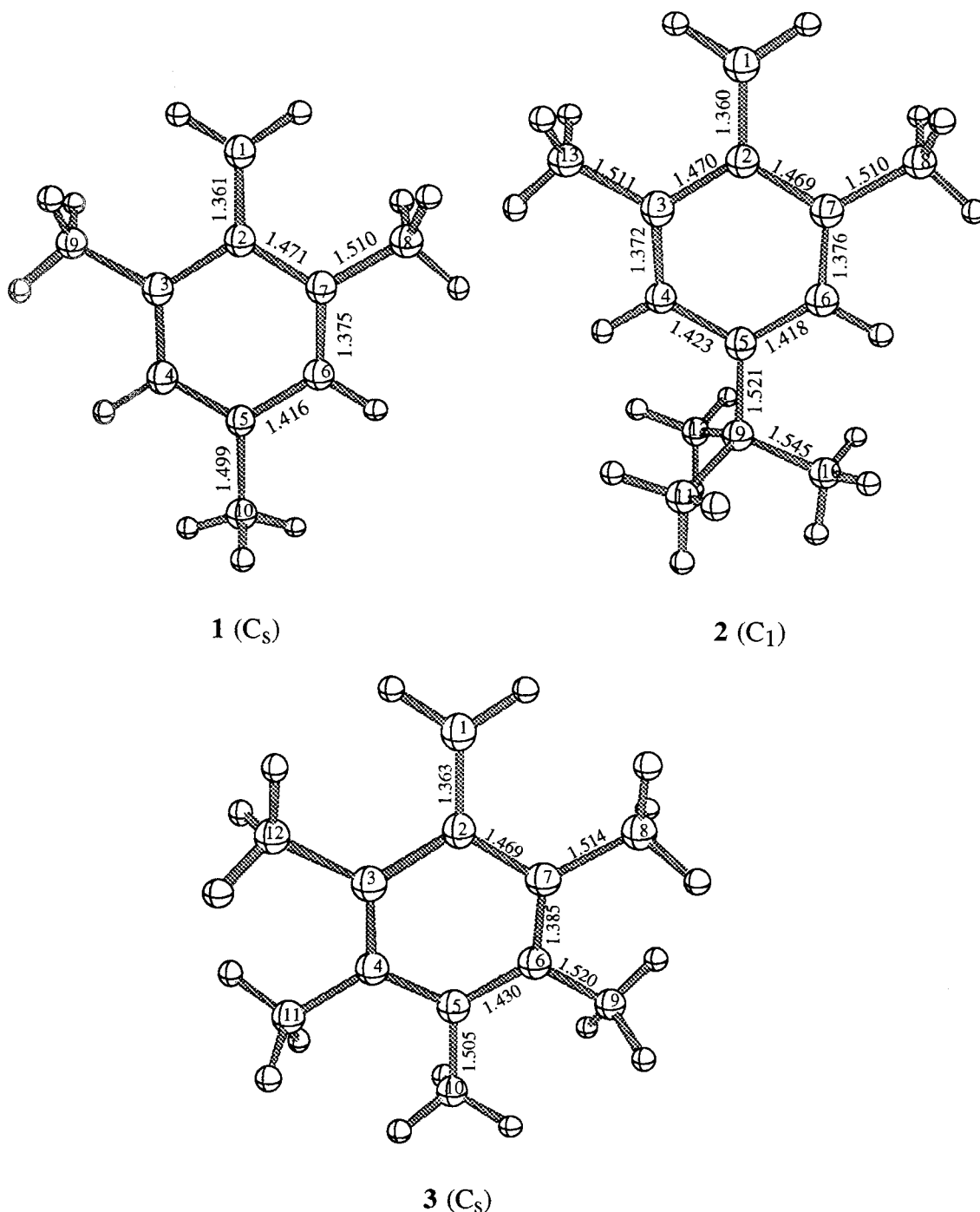
(14) Dewar, M. J. S.; Holloway, M. K. *J. Am. Chem. Soc.* **1984**, *106*, 6619.

(15) (a) Schleyer, P. v. R.; Lammertsma, K. *J. Am. Chem. Soc.* **1983**, *105*, 1049. (b) Schleyer, P. v. R.; Lammertsma, K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1321.

Table 1. Calculated and Experimental ^{13}C NMR Data for **1–6**^a

benzyl cation	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃
1	182.0 (169.5)	135.8 (142.9)	176.4 (167.0)	130.0 (133.8)	201.0 (188.5)	130.0 (133.8)	176.4 (167.1)	20.4 (19.0)	20.4 (19.0)	26.8 (25.6)			
2	180.7 (170.1)	135.7 (143.1)	173.4 (167.4)	129.0 (130.6)	214.5 (198.4)	127.3 (130.6)	178.1 (167.4)	20.8 (19.5)	27.4 (26.6)	27.6 (27.0)	27.6 (27.0)	27.6 (27.0)	20.2 (19.5)
3	179.5 (167.0)	138.5 (144.5)	173.2 (161.6)	132.8 (140.5)	200.6 (186.7)	132.8 (140.5)	173.2 (161.6)	18.6 (16.8)	15.6 (14.7)	23.4 (22.3)	15.6 (14.7)	18.6 (16.8)	
4a^b	227.5 (218.5)	136.0 (143.9)	203.9 (195.4)	131.8 (140.0)	203.9 (195.4)	136.0 (143.9)	21.3 (23.9)	211.9 (198.2)	24.4 (25.6)	24.4 (25.6)	211.9 (198.2)		
5a^b	205.0 (187.0)	133.4 (142.1)	193.4 (187.0)	115.5 (119.0)	198.7 (184.2)	131.0 (138.3)	227.1 (219.1)	23.2 (29.0)	20.6 (23.6)	213.4 (192.8)	66.4 (65.4)		
6^b	180.3	224.9	224.9	180.3	224.9	224.9							

^a At IGLO/DZ//3-21G level. ^b At IGLO/DZ/B3LYP/6-31G* level. The values in parentheses correspond to experimental values.

**Figure 1.** B3LYP/3-21G calculated structures of **1–3**.

The major resonance contribution of **4a** was also indicated by density functional theory (DFT) calculations. The B3LYP/6-31G* calculated (Figure 2) C₆–C₁₁ bond distance is 1.377

Å, which is slightly longer than that of a double bond (1.34 Å). On the other hand, C₁–C₂ bond distance is 1.451 Å, which is between those of a single (1.54 Å) and a double bond. Thus,

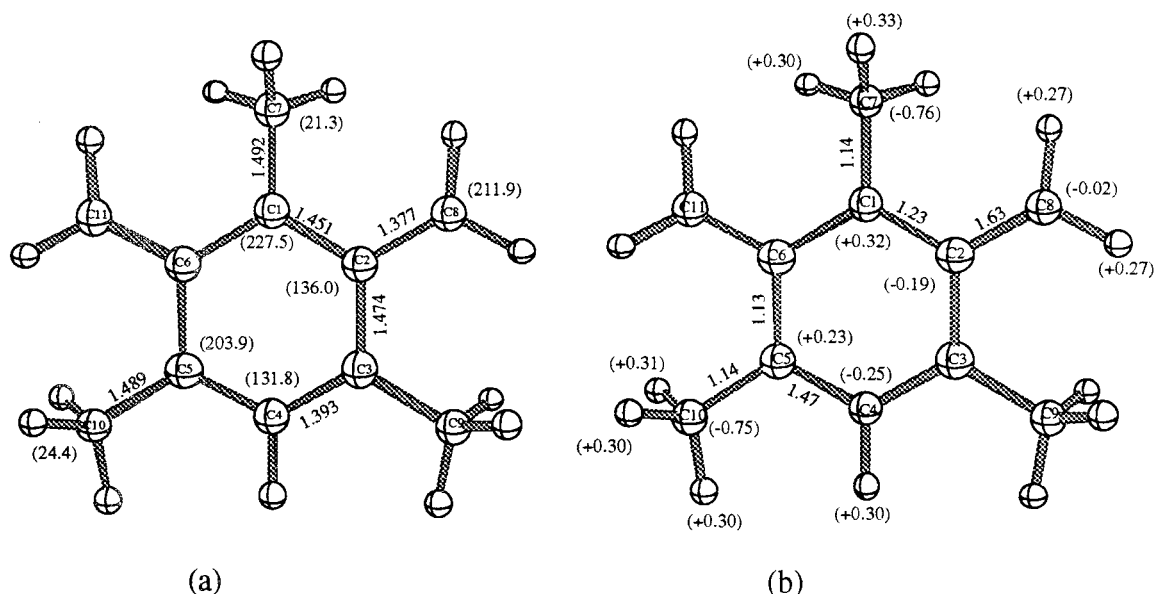


Figure 2. B3LYP/6-31G* calculated (a) bond distance and IGLO ¹³C NMR chemical shifts (in parentheses). (b) Löwdin bond order and NBO charges (in parentheses) of **4a**.

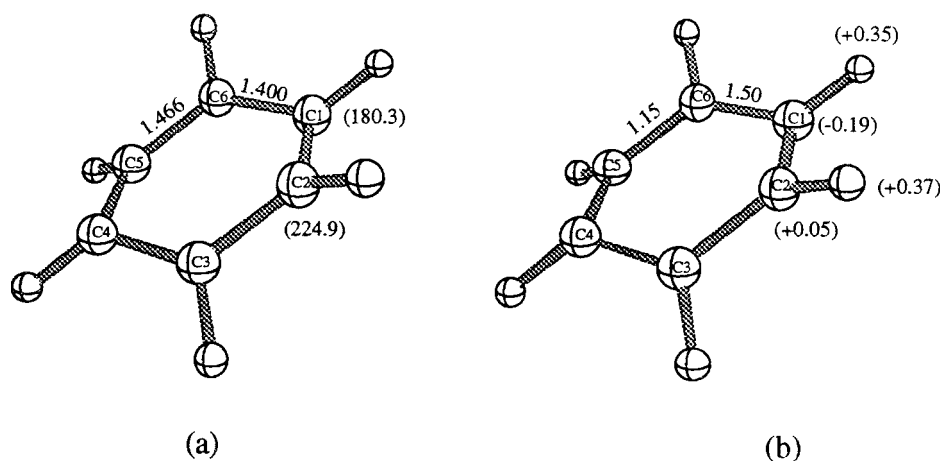


Figure 3. B3LYP/6-31G* calculated (a) bond distance and IGLO ¹³C NMR chemical shifts (in parentheses). (b) Löwdin bond order and NBO charges (in parentheses) of **6**.

one of the positive charges of the dication is asymmetrically delocalized over the C₈-C₂-C₁-C₆-C₁₁ atoms (i.e., dienyl cation). The other positive charge is delocalized among C₅-C₄-C₃ atoms (i.e., allyl cation) as the bond distance of C₃-C₄ (1.393 Å) is between those of single and double bond. So, the dication can be described as dienyl-allyl dication. These results are also in agreement with the calculated Löwdin bond orders¹¹ and natural bond orbital (NBO) charges¹² (Figure 2). IGLO calculated ¹³C NMR chemical shifts of **4a** (Figure 2) correlate well with the experimentally obtained data as shown in Scheme 3.

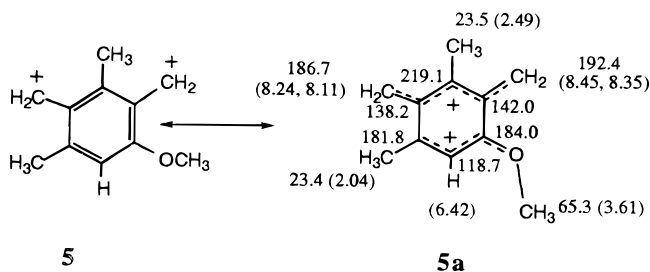
To support this argument, we also calculated the benzene dication at the B3LYP/6-31G* level. Comparison of the geometries calculated for **4a** (Figure 2) and those of calculated for **6** (Figure 3) shows considerable similarities between the two structures, although, former cation involves with a dienyl-allyl and later involves with an allyl-allyl interactions.

The ¹³C NMR spectrum of the dication 2,6-dimethyl-5-methoxy-*m*-xylyldiyl dication **5** consists of 11 well-resolved peaks at δ ¹³C 219.1 (s), 192.4 (t, $J_{C,H}$ = 170.1 Hz), 186.7 (t, $J_{C,H}$ = 169.4 Hz), 184.0 (s), 181.9 (s), 142.0 (s), 138.2 (s), 118.7 (d, $J_{C,H}$ = 176.2 Hz), 65.3 (q, $J_{C,H}$ = 155.4 Hz), 23.4 (q, $J_{C,H}$ = 133.8 Hz), 23.5 (q, $J_{C,H}$ = 133.8 Hz). The 300 MHz ¹H NMR showed absorptions at δ ¹H 8.45–8.11 (br, 4H), 6.42 (singlet, 1H), 3.61 (singlet, 3H), 2.49 (singlet, 3H), and 2.04

(singlet, 3H). The ion was found to be indefinitely stable at -78 °C. The assignment of the chemical shifts of the carbon atoms was based on their position, integrated areas, the ¹³C NMR spectral multiplicity patterns, and the C-H coupling constants of the dication.

Dienylic oxoallylic dication structure **5a** seems to be the predominant contributor of the 2,6-dimethyl-5-methoxy-*m*-xylyldiyl dication **5** based on observed NMR data. The ¹³C and ¹H (in brackets) NMR chemical shift assignments are shown on the structure **5a** in Scheme 4. The stability of the dication can also be due to the two isolated, highly stabilized dienylic and oxoallylic cationic segments in the structure **5a**.

Scheme 4



DFT/IGLO calculations also indicated that the resonance

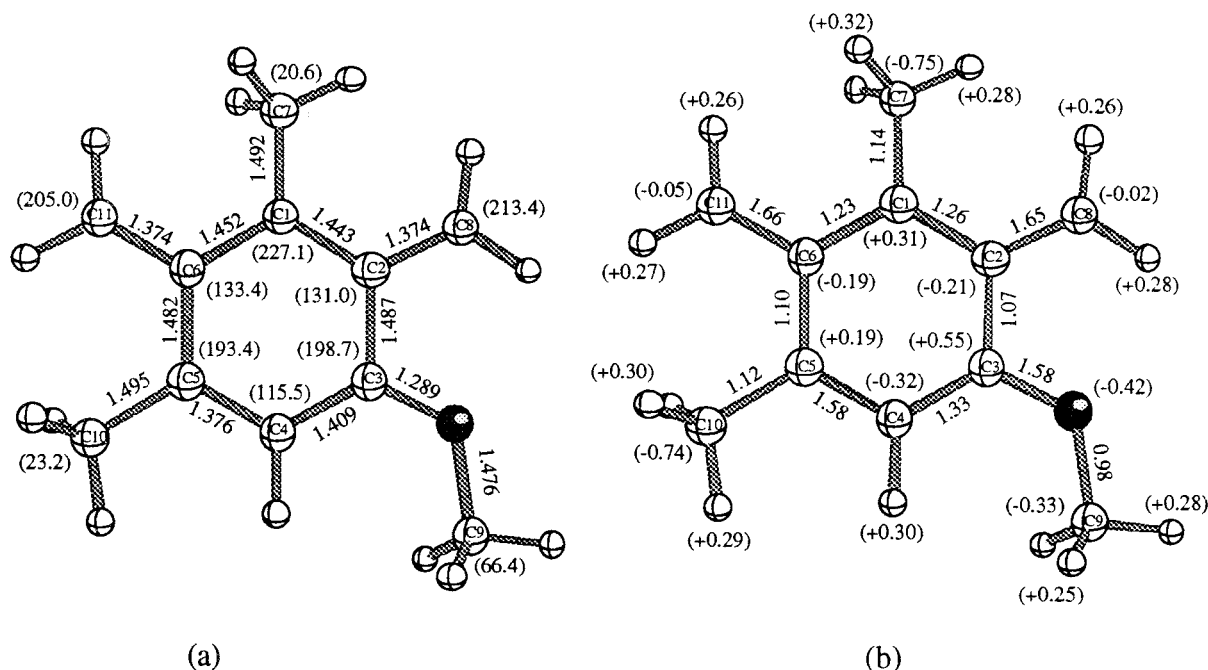
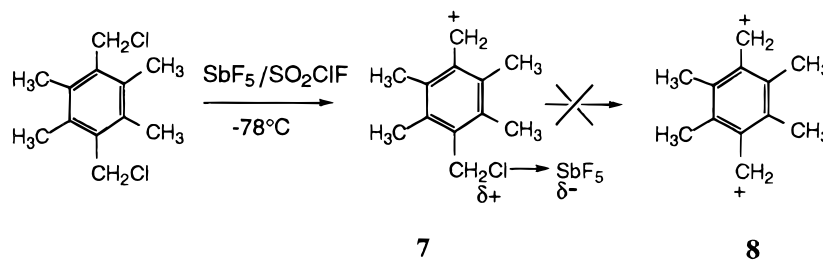


Figure 4. B3LYP/6-31G* calculated (a) bond distance and IGLO ¹³C NMR chemical shifts (in parentheses) (b) Löwdin bond order and NBO charges (in parentheses) of **5a**.

Scheme 5



structure **5a** is the predominant contributor of the dication **5**. DFT B3LYP/6-31G* calculated C_s symmetrical structure is shown in Figure 4. Both $\text{C}_6\text{--C}_{11}$ and $\text{C}_2\text{--C}_8$ bond distances are 1.374 Å, which are slightly longer than that of a double bond (1.34 Å). The $\text{C}_1\text{--C}_2$ and $\text{C}_1\text{--C}_6$ bond distances are 1.443 and 1.452 Å, respectively, which are between those of a single (1.54 Å) and a double bond. Thus, one of the positive charge of the dication is delocalized over $\text{C}_8\text{--C}_2\text{--C}_1\text{--C}_6\text{--C}_{11}$ atoms (i.e., dienylium cation). The other positive charge is delocalized among $\text{C}_5\text{--C}_4\text{--C}_3\text{--O}$ atoms (i.e., oxoallylium cation) as the bond distances of $\text{C}_3\text{--C}_4$ and $\text{C}_4\text{--C}_5$ (1.409 Å and 1.376 Å) are between those of a single and a double bond and the $\text{C}_3\text{--O}$ bond is close to that of the $\text{C}=\text{O}$ bond of carbonyl compounds (i.e., a carboxonium ion). So, the dication **5a** can be described as dienylium–oxoallylium dication. Unlike dication **4a**, the structure **5a** is perfectly planar. There is very little interaction between the dienylium and the oxoallylium parts of the dication as the $\text{C}_2\text{--C}_3$ and $\text{C}_6\text{--C}_5$ bond distances (1.487 and 1.482 Å) are close to that of a single bond. These results are also consistent with calculated Löwdin bond orders¹¹ and natural bond orbital (NBO) charges¹² of **5a** (Figure 4). Thus, the bond orders of $\text{C}_8\text{--C}_2$, $\text{C}_2\text{--C}_1$, $\text{C}_1\text{--C}_6$, and $\text{C}_6\text{--C}_{11}$ are 1.65, 1.26, 1.23, and 1.66, respectively, and the atomic charges of C8, C2, C1, C6, and C11 are -0.02 , -0.21 , $+0.31$, -0.19 , and -0.05 au, respectively, indicating charge delocalization over $\text{C}_8\text{--C}_2\text{--C}_1\text{--C}_6\text{--}$

C_{11} atoms. The $\text{C}_2\text{--C}_3$ and $\text{C}_6\text{--C}_5$ bond orders of 1.07 and 1.10, respectively, indicate little interaction between the dienylium and the oxoallylium parts of the dication. IGLO calculated ¹³C NMR chemical shifts of **5a** are also correlate very well with the experimentally obtained data (Figure 4).

Comparison of the geometries calculated for benzene dication (chair conformation) **6** (Figure 3) and for **5a** (Figure 4) also shows considerable similarities between the two structures, although the former cation involves a dienylium–allylium system whereas the latter involves an allylium–oxoallylium system.

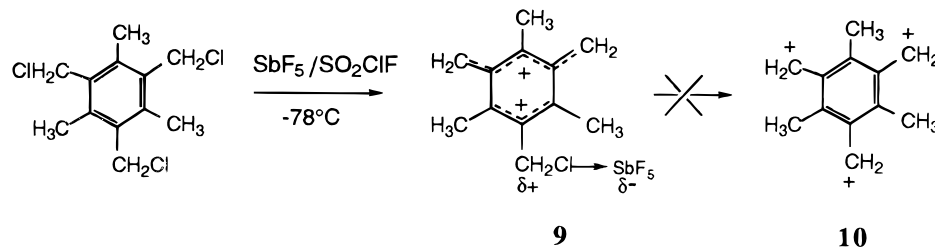
Attempted Preparation of 2,3,5,6-Tetramethylbenzene-1,4-dimethyldiyl Dication 8. In an attempt to prepare dication **8**, 2,3,5,6-tetramethyl-1,4-bis(chloromethyl)benzene was ionized in $\text{SbF}_5/\text{SO}_2\text{ClF}$ solution at -78°C . ¹³C NMR spectrum of the solution indicated, however, the formation of only monocation **7** (Scheme 5). No evidence was obtained for the formation of dication **8**. The un-ionized chloromethyl group of the monocation **7** forms a donor–acceptor complex with SbF_5 . Thus, the observed ¹³C NMR chemical shifts of $\delta^{13}\text{C}$ of positively charged benzylic carbon C1 and the CH_2Cl carbon are expectedly deshielded at $\delta^{13}\text{C}$ 170.2 and 82.9, respectively.

Attempted Preparation of 2,4,6-Trimethylmesityltriyl Trication 10. It was also attempted to prepare benzyl trication **10** by the ionization of 2,4,6-tris(chloromethyl)mesitylene in excess of SbF_5 in SO_2ClF at -78°C . ¹³C NMR spectrum of the resulting deep orange-red colored solution indicated, however, only the formation of only dication **9** (Scheme 6). There is no indication for the formation of trication **10**. The un-ionized

(16) Fuson, R. C.; Denton, J. J.; Kneisley, J. W. *J. Am. Chem. Soc.* **1941**, *63*, 2652.

(17) Aitken, R. R.; Badger, G. M.; Cook, J. W. *J. Chem. Soc.* **1950**, 331.

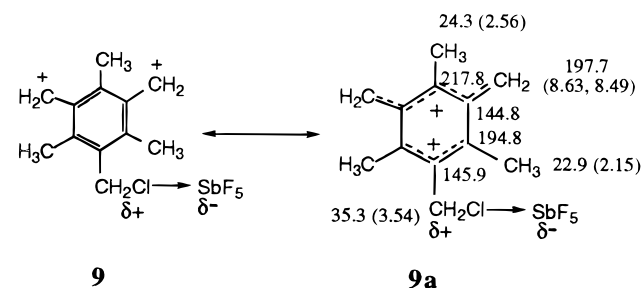
Scheme 6



chloromethyl group of dication **9** seems to form a very weak donor–acceptor complex with SbF_5 . Similar results were obtained when the ionization was carried out in more acidic $\text{HF}:\text{SbF}_5/\text{SO}_2\text{ClF}$ medium.

The ^{13}C NMR spectrum of the dication **9** consists of eight peaks at δ ^{13}C 217.8 (s), 197.7 (t), 194.8 (s), 145.9 (s), 144.8 (s), 35.3 (t), 24.3 (q), 22.9 (q). The ^1H NMR showed absorptions at δ ^1H 8.63–8.49 (br, 4H), 3.54 (singlet, 2H), 2.56 (singlet, 3H), and 2.15 (singlet, 3H). Based on the observed NMR data the dienylic allylic dication structure **9a** seems to be the major contributor of the dication **9** (Scheme 7). **9a** is very similar to structure **4a**.

Scheme 7



Conclusions

Several substituted benzylic mono- and dications were prepared and investigated by ^1H and ^{13}C NMR spectroscopy as well as by DFT/IGLO calculations. IGLO calculated ^{13}C NMR chemical shifts agree well with the experimental data. Combined experimental and theoretical study suggest that **1a** is the major resonance contributor to the overall structure of the 2,4,6-trimethylbenzyl monocation **1**. Similar results were also found for the 2,4,6-dimethyl-4-*tert*-butylbenzyl **2** and 2,3,4,5,6-pentamethylbenzyl cation **3**. The studies also suggest that **4a** is the predominant canonical contributor to the overall structure of the 2,6-dimethylmesityldiyl dication **4** wherein the dienylic and allylic cation units are insulated from each other. Similar studies indicated that **5a** is the predominant canonical contributor to the overall structure of 2,6-dimethyl-5-methoxy-*m*-xylyldiyl dication **5** wherein the dienylic and oxoallylic cation units are again insulated from each other. Attempts to generate 2,3,5,6-tetramethylbenzene-1,4-dimethyldiyl dication **8** was, however, not successful as was that to generate the 2,4,6-trimethylmesityltriyl trication **10** by ionization of 2,4,6-bis(chloromethyl)-mesitylene. The resulting ion was characterized as chloromethyl substituted dication **9**.

Experimental Section

SbF_5 and SO_2ClF were doubly distilled prior to use in the preparation of the ions. 2,4,6-Trimethylbenzyl chloride, 2,3,4,5,6-pentamethylbenzyl chloride, 2,6-bis(chloromethyl)mesitylene, 5-*tert*-butyl-*m*-xylene, 2,3,5,6-tetramethylbenzyl chloride, 3,5-dimethylanisole, and 2,4,6-bis(chloromethyl)mesitylene are commercial samples of the highest purity and were used without further purification. ^1H and ^{13}C NMR spectra were obtained on a spectrometer equipped with a variable-temperature

probe at 300 and 75.4 MHz, respectively. ^1H and ^{13}C NMR spectra were obtained with respect to TMS by using an acetone- d_6 capillary as external standard.

2,6-Dimethyl-4-*tert*-butylbenzyl Chloride.¹⁶ To 7.3 g (45 mmol) of 5-*tert*-butyl-*m*-xylene in 38 mL of concentrated hydrochloric acid was added 15 g of formalin (37% formaldehyde in water). This mixture was heated at 80°C for 48 h with vigorous stirring. The solution was allowed to cool, and the solid material was filtered and washed with water. The solid material was then taken up in dichloromethane, washed with sodium carbonate solution, and dried over anhydrous potassium carbonate. Removal of dichloromethane left 6.97 g of a white solid. Three recrystallizations from hexanes gave 4.39 g of pure compound, 46%. MS (m/z , 70 eV, EI): 210 (M^+ , 15.0), 195 (66.2), 175 (49.3), 119 (63.1), 77 (65.2), 51 (100); $^1\text{H-NMR}$ (CDCl_3) δ = 1.28 (s, 9H, CH_3), 2.42 (s, 6H, CH_3), 4.64 (s, 2H, CH_2), 7.06 (s, 2H, CH); ^{13}C NMR 151.46, 136.99, 131.01, 125.42, 41.13, 34.32, 31.19, 19.50.

3,6-Bis(chloromethyl)durene.¹⁷ A mixture of 2,3,5,6-tetramethylbenzyl chloride (4.11 g, 23 mmol), concentrated hydrochloric acid (18.8 mL), and formalin (7.5 g) was heated at 90°C for 12 h with vigorous stirring. The solution was then filtered and washed with water. The solid material was taken up in dichloromethane, washed with sodium carbonate solution followed with water, and dried over anhydrous potassium carbonate. Removal of dichloromethane left 3.59 g of a white solid. Three recrystallizations from hexanes gave 1.36 g of pure compound, 26%, mp 194–195°C. MS (m/z , 70 eV, EI): 230 (M^+ , 2.9), 195 (75.5), 129 (100), 115 (89.8), 91 (89.8), 77 (80), 51 (78.9); $^1\text{H-NMR}$ (CDCl_3) δ = 2.34 (s, 12H, CH_3), 4.69 (s, 4H, CH_2); ^{13}C NMR 134.54, 134.02, 42.21, 15.89.

2,4-Bis(chloromethyl)-3,5-dimethylanisole. A mixture of 3,5-dimethylanisole (6.13 g, 45 mmol), concentrated hydrochloric acid (38 mL), and formalin (15 g) was heated at 30 °C for 12 h with vigorous stirring. The solution was then filtered and washed with water. The visible solid material was taken up in dichloromethane, washed with sodium carbonate solution followed with water, and dried over anhydrous potassium carbonate. Removal of dichloromethane left 4.68 g of a white solid. Two recrystallizations from hexanes gave 3.57 g of pure compound, 43%, mp 129–130 °C. MS (m/z , 70 eV, EI): 232 (M^+ , 6.2), 197 (72.4), 117 (48.9), 91 (100), 77 (73), 65 (46.3), 51 (87.1); $^1\text{H-NMR}$ (CDCl_3) δ = 2.44 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 4.67 (s, 2H, CH_2), 4.75 (s, 2H, CH_2), 6.62 (s, 1H, CH); ^{13}C NMR 157.43, 139.73, 138.91, 126.90, 122.66, 110.70, 55.68, 41.60, 38.26, 20.11, 14.63.

Preparation of Ions. Approximately 1.5 mL of 50% v/v solution of SbF_5 in SO_2ClF was placed into a 5 mm NMR tube and cooled to -78 °C in a dry ice/acetone bath. The appropriate benzyl chloride (~30 mg) was carefully added to the solution at -78 °C. The ensuing mixture was vigorously stirred (Vortex stirrer) under periodic cooling, and samples were transferred to NMR studies.

NMR Spectroscopy. ^1H and ^{13}C NMR spectra were recorded on a Varian Associates Model VXR-300 spectrometer, equipped with a 5 mm variable temperature broad band probe. All spectra were obtained, operating with an internal lock provided by an acetone- d_6 capillary. ^1H , ^{13}C resonances were referenced to external (capillary) tetramethylsilane.

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