

## 2,6-Dimethylmesitylene-2,6-diyl Dication, a Unique Dienyl–Allyl Dication and Its Comparison with Bisallylic Benzene Dication<sup>1</sup>

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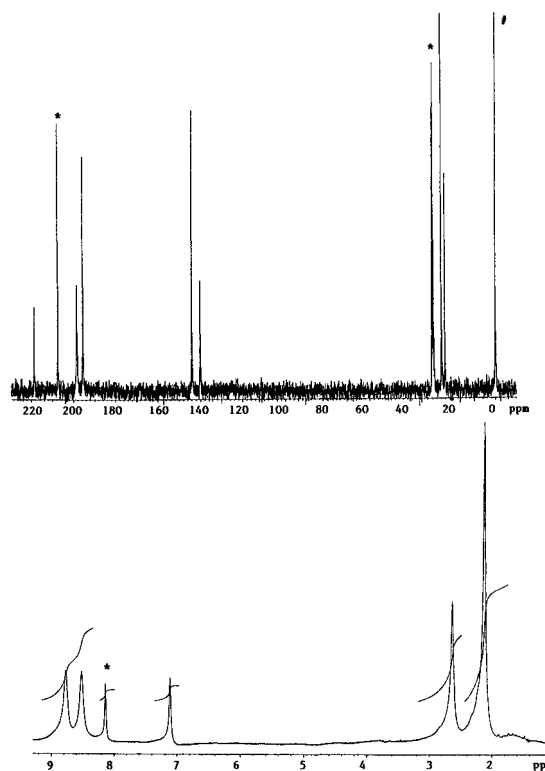
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In the past two decades the study of long-lived carbocations has been of considerable interest.<sup>2</sup> Previous studies on carbocations have shown that in the absence of aryl stabilization of the carbocation centers, persistent (long-lived) dipositive ions can be generated only if the carbocation centers are separated by at least two carbon atoms and the carbenium centers are tertiary.<sup>3</sup> Recently, we reported successful characterization of 2,10-*para*-[3<sup>2</sup>.5<sup>6</sup>]octahedranedimethyl dication, a novel bis-cyclopropylmethyl cation.<sup>4</sup> Whereas a series of ring-substituted benzylic monocations (arylcarbenium ions) have been observed,<sup>5</sup> long-lived 1,3-dimethylbenzene-1,3-diyl dications, wherein the carbocation centers are both primary, are presently unknown. Using methods developed in our previous studies that allowed the preparation of monocarbocationic intermediates under long-lived, stable ion conditions,<sup>6</sup> we now wish to report the preparation, NMR spectroscopic characterization, and DFT/IGLO study of the 2,6-dimethylmesitylene-2,6-diyl dication **2** and its unique structural nature.

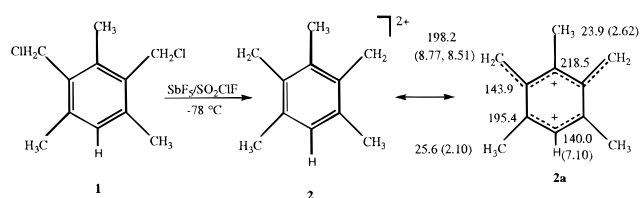
Ionization of 2,6-bis(chloromethyl)mesitylene (**1**) in 5-fold excess of SbF<sub>5</sub> in SO<sub>2</sub>ClF at –78 °C resulted in a deep red colored solution (Scheme 1).<sup>7</sup> The 75 MHz <sup>13</sup>C NMR spectrum exhibited seven well-resolved, peaks at δ 218.5 (s), 198.2 (t, *J*<sub>C,H</sub> = 170.3 Hz), 195.4 (s), 143.9 (s), 140.0 (d, *J*<sub>C,H</sub> = 177.3 Hz), 25.6 (q, *J*<sub>C,H</sub> = 131.9 Hz), and 23.9 (q, *J*<sub>C,H</sub> = 132.3 Hz). The 300 MHz <sup>1</sup>H NMR showed absorptions at δ 8.77 (br, 2H), 8.51 (br, 2H), 7.10 (s, 1H), 2.62 (s, 3H), and 2.10 (s, 6H). The <sup>1</sup>H and <sup>13</sup>C NMR spectra are shown in Figure 1. The ion is remarkably stable even at –10 °C. On the basis of the observed NMR data, a dienyl allylic dication system (**2a**) appears to be the major contributor to the structure **2**.

The <sup>1</sup>H (in brackets) and <sup>13</sup>C NMR chemical shift assignments are shown on the structure **2a** in Scheme 1. The remarkable



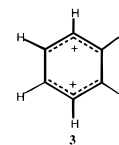
**Figure 1.** <sup>13</sup>C (upper, \* acetone-*d*<sub>6</sub>, # TMS) and <sup>1</sup>H (lower, \* acid peak) NMR spectra of 2,6-dimethylmesitylene-2,6-diyl dication **2** in SbF<sub>5</sub>/SO<sub>2</sub>ClF at –78 °C.

### Scheme 1



stability of the dication can be attributed to highly stabilized dienyl-allyl dication nature (i.e., **2a**).

Dicationic structure **2a** is reminiscent of the bisallylic benzene dication **3**. The benzene dication **3** is experimentally still elusive although bi- and polycyclic analogs were obtained by two-electron oxidation of the corresponding arenes by SbF<sub>5</sub>.<sup>8</sup>



MINDO/3 calculations by Dewar et al.<sup>9a</sup> showed that the benzene dication **3** favors a C<sub>2h</sub> chair conformation as the most stable form, with essentially isolated allyl cation units. Schleyer et al. subsequently found<sup>9b</sup> that **3** is subject to Jahn–Teller distortion upon optimization forming a double allylic cation. According to Schleyer et al.,<sup>9c</sup> the uncoupling of the allyl units in **3** tends to keep the pairs of π electrons as far apart from one another as possible, thus minimizing the repulsions between

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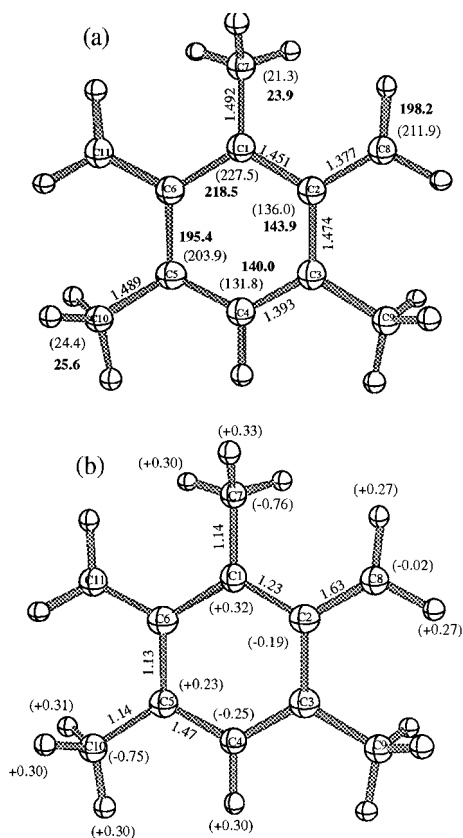
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(7) (a) The dication **2** was prepared by careful addition of the precursor **1** (~30 mg) to a well-stirred 1.5 mL sample of a 50% v/v solution of SbF<sub>5</sub> in SO<sub>2</sub>ClF at –78 °C.



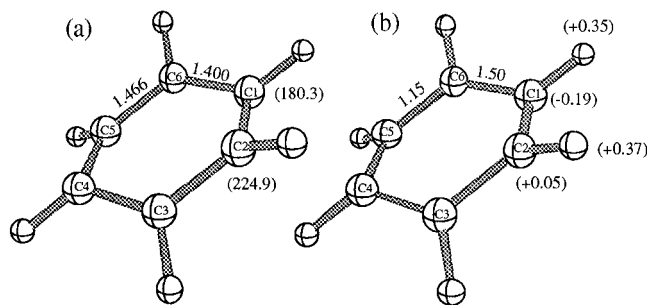
**Figure 2.** B3LYP/6-31G\*-calculated (a) bond distance and IGLO/DZ <sup>13</sup>C NMR chemical shifts (in parentheses); experimental shifts are given in bold. (b) Löwdin bond order and NBO charges (in parentheses) of **2a**.

them. This leads to unequal bond lengths in the ring and forces the ring to be distorted from planarity.

The predominant contribution of **2a** to the structure of the dication **2** as observed by NMR in superacids is further supported by density functional theory (DFT)<sup>10</sup>/IGLO<sup>11</sup> calculations. The geometry was fully optimized at the DFT B3LYP/6-31G\* level in its *C*<sub>1</sub> symmetry. However, the final geometry **2a** was found to be very close to *C*<sub>s</sub> symmetry (Figure 2). The C<sub>6</sub>–C<sub>11</sub> bond distance is 1.377 Å, slightly longer than that of a double bond (1.34 Å). On the other hand, the C<sub>1</sub>–C<sub>2</sub> bond distance is 1.451 Å, between those of a single (1.54 Å) and a double bond. Thus, one of the positive charge of the dication is asymmetrically delocalized over C<sub>8</sub>–C<sub>2</sub>–C<sub>1</sub>–C<sub>6</sub>–C<sub>11</sub> atoms (i.e., dienyl cation). The second positive charge is delocalized among C<sub>5</sub>–C<sub>4</sub>–C<sub>3</sub> atoms (i.e., allyl cation), since the bond distance of C<sub>3</sub>–C<sub>4</sub> (1.393 Å) is between those of single and double bond. Consequently, the dication **2a** can be described as dienyl–allyl dication. The structure can also be

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

considered as that of a substituted benzene dication. Compound **2a** is slightly distorted from planarity since the C<sub>1</sub>–C<sub>2</sub>–C<sub>3</sub>–C<sub>4</sub> dihedral angle was found to be 3.0°. There seems to be very little interaction between dienyl and allyl units of the dication since the C<sub>2</sub>–C<sub>3</sub> bond distance (1.474 Å) is close to that of a single bond. These results are also consistent with calculated Löwdin bond orders<sup>12</sup> and natural bond orbital (NBO) charges<sup>13</sup> of **2a** (Figure 2). Thus, the bond orders of C<sub>6</sub>–C<sub>11</sub> and C<sub>1</sub>–C<sub>6</sub> are 1.63 and 1.23, respectively, and the atomic charges of C<sub>1</sub>, C<sub>2</sub>, and C<sub>3</sub> are +0.32, –0.19, and –0.02 au are again indicating asymmetrical charge delocalization over C<sub>8</sub>–C<sub>2</sub>–C<sub>1</sub>–C<sub>6</sub>–C<sub>11</sub> atoms. The C<sub>2</sub>–C<sub>3</sub> bond order of 1.13 indicates only little interaction between dienyl and allyl units of the dication. IGLO, calculated <sup>13</sup>C NMR chemical shifts of **2a** are also correlate well with the experimentally obtained data (see Figure 2).

The calculated <sup>13</sup>C NMR chemical shifts of carbocationic center (CH<sub>2</sub> carbon) of **2a** is 13.7 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.<sup>14</sup> However, GIAO-MP2 calculations using ACES II program<sup>15</sup> are presently limited to only small-size molecules.

To substantiate the structural nature of **2a** and **3**, we also carried out calculations on the benzene dication system at the same DFT B3LYP/6-31G\* level. Optimized structure of the dication is the *C*<sub>2h</sub> symmetrical **3** (chair conformation) with substantial distortion from planarity (C<sub>3</sub>–C<sub>4</sub>–C<sub>5</sub>–C<sub>6</sub> dihedral angle is 31.6°). Comparison of the geometries calculated for **2a** (Figure 2) and those of calculated for **3** (Figure 3) shows considerable similarities, and although **2a** involves a dienyl–allyl dication, the latter encompasses an allyl–allyl dication.

In conclusion, we have succeeded in the preparation and characterization of the first persistent (stable) dienyl–allyl dication, the 2,6-dimethylmesitylene-2,6-diyl dication **2**, and study its structure by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies. DFT/IGLO theoretical NMR chemical shift calculations gave excellent correlation with the experimental data. The combined experimental and theoretical approach support structure **2a** wherein the dienyl and allylic cation units are insulated from each other not unlike what is theoretically calculated for the related benzene dication **3**.

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