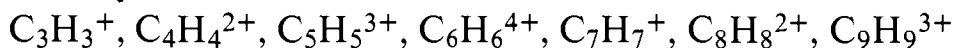


# On the Limits of Stability of Multiply Charged

## Monocyclic Aromatic Cations:

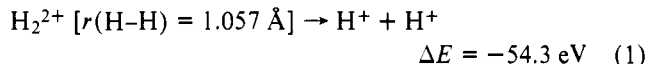


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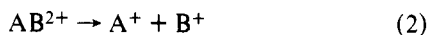
Contribution from the Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600, Australia. Received April 22, 1977

**Abstract:** The aromatic tetramethylcyclobutadiene [ $\text{C}_4(\text{CH}_3)_4^{2+}$ ] and 1,3,5,7-tetramethylcyclooctatetraene [ $\text{C}_8\text{H}_4(\text{CH}_3)_4^{2+}$ ] dications have recently been prepared experimentally by Olah and co-workers. To complement their work and to investigate the possibility of a small aromatic trication, ab initio theoretical studies have been carried out. Self-consistent field (SCF) theory has been used in conjunction with minimal (STO-3G) and split-valence (4-31G) basis sets to examine the structures and stabilities of the cations  $\text{C}_3\text{H}_3^+$ ,  $\text{C}_4\text{H}_4^{2+}$ ,  $\text{C}_5\text{H}_5^{3+}$ ,  $\text{C}_6\text{H}_6^{4+}$ ,  $\text{C}_7\text{H}_7^+$ ,  $\text{C}_8\text{H}_8^{2+}$ ,  $\text{C}_9\text{H}_9^{3+}$ , and  $\text{C}_4(\text{CH}_3)_4^{2+}$ . Exothermic (by about 30 kcal mol<sup>-1</sup>) fragmentation reactions are found for the unsubstituted  $\text{C}_4\text{H}_4^{2+}$  and  $\text{C}_8\text{H}_8^{2+}$  dications. The possibility of observing these species will depend on the activation energies for the fragmentation reactions. It is considered unlikely that the  $\text{C}_5\text{H}_5^{3+}$  and  $\text{C}_9\text{H}_9^{3+}$  trications or the  $\text{C}_6\text{H}_6^{4+}$  tetracation will be observable because of the existence of fragment systems with substantially (>150 kcal mol<sup>-1</sup>) lower energy.

Small doubly charged molecular ions are often subject to spontaneous dissociation. This is because the second molecular ionization potential (IP) may be considerably greater than the first IP of either of the neutral fragments. The simplest example is molecular hydrogen; although it represents the extreme,  $\text{H}_2$  has the decided advantage of precisely determined thermochemical data. While the first IP of  $\text{H}_2$  is 15.6 eV, the second is enormous, 70.7 eV.<sup>3,4</sup> The latter energy corresponds to vertically removing an electron from  $\text{H}_2^+$  at its equilibrium internuclear separation, 1.057 Å. This means that the process



is tremendously exothermic, since the ionization potential of each H atom is only 13.6 eV. More generally, for the fragmentation process



the exothermicity is given by

$$\Delta E = [D_0(\text{AB}) + \text{IP}(\text{A}) + \text{IP}(\text{B})] - [\text{IP}(\text{AB}) + \text{IP}(\text{AB}^+)] \quad (3)$$

For larger molecular systems, of course, second ionization potentials can sometimes be rather low, owing to the possibility of delocalizing the second charge.<sup>5</sup> Perhaps the most fascinating examples studied to date are the aromatic dications recently reported by Olah and co-workers.<sup>6,7</sup> These dications are endowed with  $(4n + 2)$   $\pi$  electrons and their planar monocyclic structures are expected to be especially stable.<sup>8,9</sup> At least four cyclobutadiene dications [ $n = 0$  in the  $(4n + 2)$  formula] have been prepared:<sup>6</sup> the tetraphenyl, 1,2-difluoro-3,4-diphenyl, 1,2-diphenyl, and tetramethyl species. Although some evidence was obtained for the existence of the 1,2-dimethylcyclobutadiene dication, all efforts to prepare the parent (unsubstituted)  $\text{C}_4\text{H}_4^{2+}$  were unsuccessful. Research on the  $6\pi$  systems  $\text{C}_8\text{R}_8^{2+}$  is much more recent in origin, with only the 1,3,5,7-tetramethylcyclooctatetraene dication having been reported thus far, by Olah, Stalar, and Paquette.<sup>7</sup>

The present study is designed to suggest theoretical limits to the number of positive charges a simple monocyclic aromatic cation may accommodate. Since even the relatively small  $\text{C}_4\text{R}_4$  systems can support a +2 charge, an initial motivation was the possibility that the much larger  $6\pi$  electron species  $\text{C}_9\text{R}_9^{3+}$  might provide a stable trication, given suitable substituents.

We begin with a simple Hückel analysis of the problem and then proceed to detailed ab initio self-consistent field (SCF) calculations. Many of the cations considered here are hypothetical, not having yet been observed experimentally. However, we do make direct contact with experiment for several species, including the  $\text{C}_4(\text{CH}_3)_4^{2+}$  dication.

### Theoretical Aspects

A convenient starting point in the study of aromatic cations is Hückel molecular orbital theory. Derivation of the Hückel energies is trivial<sup>10</sup> and is reproduced for the  $\text{C}_3\text{H}_3^+$  to  $\text{C}_9\text{H}_9^{3+}$  systems in Figure 1. Two interesting points emerge from the Hückel molecular orbitals. The first concerns the bonding characteristics of the unoccupied orbitals. For the neutral ( $\text{C}_6\text{H}_6$ ) and monocation ( $\text{C}_3\text{H}_3^+$  and  $\text{C}_7\text{H}_7^+$ ) systems, only *antibonding* orbitals are unoccupied. For the dications ( $\text{C}_4\text{H}_4^{2+}$  and  $\text{C}_8\text{H}_8^{2+}$ ), the unoccupied manifold includes *nonbonding* orbitals. On the other hand, the trications,  $\text{C}_5\text{H}_5^{3+}$  and  $\text{C}_9\text{H}_9^{3+}$ , have unoccupied *bonding* orbitals with energies of  $0.618\beta$  and  $0.347\beta$ , respectively. These observations apply generally to the Hückel molecular orbitals of neutral, mono-, di- and trication annulene systems. In particular, the trications will always contain unoccupied bonding orbitals in the Hückel analysis and, although the binding energy of these unoccupied orbitals decreases with increasing ring size (cf.  $\text{C}_5\text{H}_5^{3+}$  and  $\text{C}_9\text{H}_9^{3+}$  above), the situation is a nonoptimal one.

The second relevant result from the Hückel analysis comes from Hückel delocalization energies (HDE's, Table I) defined<sup>10</sup> as the difference between the Hückel energy,  $E(\text{Hückel})$ , and the energy,  $E(\text{Kekule})$ , of the corresponding localized (Kekule) structure:

$$\text{HDE} = -[E(\text{Hückel}) - E(\text{Kekule})] \quad (4)$$

Positive values for HDE are obtained in all cases reflecting the conjugative stabilization for these  $(4n + 2)$   $\pi$ -electron systems. For the  $2\pi$ -electron ions  $\text{C}_3\text{H}_3^+$ ,  $\text{C}_4\text{H}_4^{2+}$ ,  $\text{C}_5\text{H}_5^{3+}$ , and  $\text{C}_6\text{H}_6^{4+}$ , the HDE's are constant at  $-\beta$ . On the other hand, the HDE's actually increase along the sequence of  $6\pi$ -electron systems  $\text{C}_6\text{H}_6$ ,  $\text{C}_7\text{H}_7^+$ ,  $\text{C}_8\text{H}_8^{2+}$ , and  $\text{C}_9\text{H}_9^{3+}$ . However, although the Hückel analysis predicts that all these species should be significantly more stable than localized model systems, it does not take into account, inter alia, the electrostatic repulsion in the multiply charged ions. Clearly, the electrostatic repulsion makes an important contribution to the forces which decide whether the multiply charged ion is stable or is likely

**Table I.** Hückel Delocalization Energies (HDE's)

Species	HDE	Species	HDE
C <sub>3</sub> H <sub>3</sub> <sup>+</sup>	-2β	C <sub>6</sub> H <sub>6</sub>	-2β
C <sub>4</sub> H <sub>4</sub> <sup>2+</sup>	-2β	C <sub>7</sub> H <sub>7</sub> <sup>+</sup>	-2.988β
C <sub>5</sub> H <sub>5</sub> <sup>3+</sup>	-2β	C <sub>8</sub> H <sub>8</sub> <sup>2+</sup>	-3.656β
C <sub>6</sub> H <sub>6</sub> <sup>4+</sup>	-2β	C <sub>9</sub> H <sub>9</sub> <sup>3+</sup>	-4.128β

**Table II.** Calculated Total Energies (Hartrees) for *D<sub>nh</sub>* Structures

Species	STO-3G/STO-3G	4-31G/STO-3G	4-31G/4-31G
C <sub>3</sub> H <sub>3</sub> <sup>+</sup>	-113.62032 <sup>a</sup>	-114.81364 <sup>a</sup>	-114.81645
C <sub>4</sub> H <sub>4</sub> <sup>2+</sup>	-151.08124	-152.65142	-152.65773
C <sub>5</sub> H <sub>5</sub> <sup>3+</sup>	-188.33192	-190.29635	
C <sub>6</sub> H <sub>6</sub> <sup>4+</sup>	-225.39056	-227.74010	
C <sub>6</sub> H <sub>6</sub>	-227.89136	-230.37722	
C <sub>7</sub> H <sub>7</sub> <sup>+</sup>	-265.66842	-268.51517	
C <sub>8</sub> H <sub>8</sub> <sup>2+</sup>	-303.17350		
C <sub>9</sub> H <sub>9</sub> <sup>3+</sup>	-340.47764		

<sup>a</sup> From ref 15a.

to fragment to smaller species. In order to predict the likely stability of these systems, we must therefore turn to a somewhat higher level of theory.

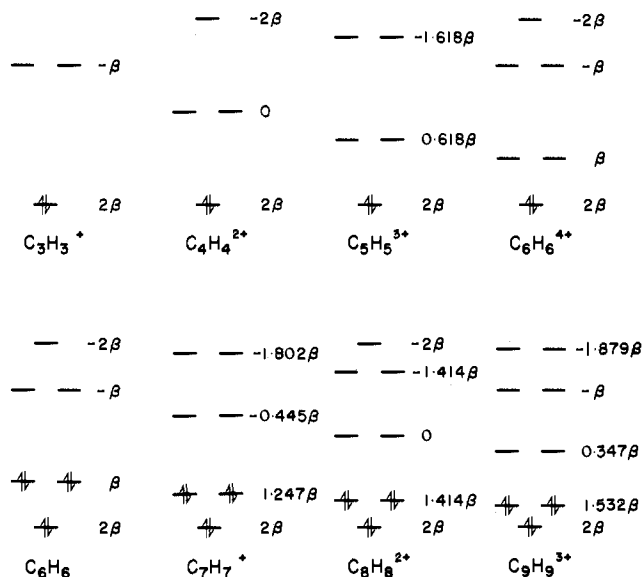
To this end, we have carried out ab initio LCAO SCF molecular orbital calculations using the Gaussian 70 system of programs.<sup>11</sup> In a first series of calculations (STO-3G/STO-3G), the minimal STO-3G basis set<sup>12</sup> was used to derive optimum STO-3G values of the C-C and C-H lengths in *D<sub>nh</sub>* structures of all the C<sub>*n*</sub>H<sub>*n*</sub><sup>*m*+</sup> systems. For systems up to the size of C<sub>7</sub>H<sub>7</sub><sup>+</sup>, single calculations (4-31G/STO-3G) on the STO-3G optimized structures were also carried out with the split-valence 4-31G basis set<sup>13</sup> in order to make more reliable energetic comparisons. Finally, the structures of the smallest cations, C<sub>3</sub>H<sub>3</sub><sup>+</sup> and C<sub>4</sub>H<sub>4</sub><sup>2+</sup>, were reoptimized with the 4-31G basis set (4-31G/4-31G) for comparison with the STO-3G structures. The STO-3G and 4-31G basis sets have both been used extensively in previous studies of neutral hydrocarbons and related carbocations.<sup>14-16</sup>

Additional calculations were performed for the C<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub><sup>2+</sup> dication, one of the experimentally observed systems, and for comparison for C<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub><sup>+</sup> and C(CH<sub>3</sub>)<sup>+</sup>. In these calculations the rings were assumed to have their optimum (STO-3G) unsubstituted structures and the methyl substituents were taken with standard<sup>17</sup> lengths and angles. The CH<sub>3</sub>-substrate bond lengths were optimized in each case. The orientation of the methyl substituents is unlikely to significantly affect the calculated energies in any of these three systems. The chosen orientations lead to overall molecular symmetries of C<sub>4h</sub> [C<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub><sup>2+</sup>], C<sub>3h</sub> [C<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>], and C<sub>3v</sub> [C(CH<sub>3</sub>)<sup>+</sup>].

## Results and Discussion

Calculated total energies and bond lengths are presented in Tables II and III, respectively.

**Bond Lengths.** The STO-3G C-C length for the cyclopropenyl cation (C<sub>3</sub>H<sub>3</sub><sup>+</sup>) has been reported previously.<sup>15a</sup> Experimental bond lengths<sup>18</sup> (1.363 and 1.373 Å) for derivatives of C<sub>3</sub>H<sub>3</sub><sup>+</sup> lie between our STO-3G (1.377 Å) and 4-31G (1.361 Å) values. For benzene, our STO-3G bond lengths of 1.387 (C-C) and 1.084 Å (C-H) are close to the experimental values<sup>19</sup> of 1.397 and 1.084 Å, respectively.<sup>20</sup> Of the other species examined here, experimental structural data are available only for the tropylium cation. Our C-C length for the tropylium cation is close to the theoretical value reported recently<sup>15e</sup> for a partially optimized structure. The experimental C-C length determined<sup>21</sup> from data for tropylium perchlorate seems much too long and may be associated with experimental difficulties due to rotation of the cation in the

**Figure 1.** Energies of Hückel molecular orbitals.**Table III.** Theoretical Bond Lengths (Å) for *D<sub>nh</sub>* Structures

Species	STO-3G		4-31G	
	C-C	C-H	C-C	C-H
C <sub>3</sub> H <sub>3</sub> <sup>+</sup>	1.377 <sup>a</sup>	1.095 <sup>a</sup>	1.361	1.064
C <sub>4</sub> H <sub>4</sub> <sup>2+</sup>	1.467	1.119	1.443	1.077
C <sub>5</sub> H <sub>5</sub> <sup>3+</sup>	1.501	1.136		
C <sub>6</sub> H <sub>6</sub> <sup>4+</sup>	1.537	1.151		
C <sub>6</sub> H <sub>6</sub>	1.387	1.083		
C <sub>7</sub> H <sub>7</sub> <sup>+</sup>	1.398	1.089		
C <sub>8</sub> H <sub>8</sub> <sup>2+</sup>	1.415	1.097		
C <sub>9</sub> H <sub>9</sub> <sup>3+</sup>	1.436	1.104		

<sup>a</sup> From ref 15a.

crystal.<sup>8b,22</sup> For the two cations for which we have both STO-3G and 4-31G bond lengths, our results suggest that the former may be slight overestimates, the error being greater for C-H than for C-C lengths.

Comparison of bond lengths in the series of 2π-electron cations shows a monotonic increase in lengths as we proceed from C<sub>3</sub>H<sub>3</sub><sup>+</sup> to C<sub>6</sub>H<sub>6</sub><sup>4+</sup>. The carbon-carbon length in C<sub>3</sub>H<sub>3</sub><sup>+</sup> is slightly shorter than the "typical" aromatic value as typified by benzene while that in C<sub>6</sub>H<sub>6</sub><sup>4+</sup> is close to the STO-3G C-C single bond length (1.538 Å) in ethane.<sup>14a</sup> These results are not unexpected since the two bonding π electrons have to be shared among an increasing number of bonds. The large increases in C-C length predicted for C<sub>4</sub>H<sub>4</sub><sup>2+</sup> compared with C<sub>3</sub>H<sub>3</sub><sup>+</sup> (0.092 Å with STO-3G and 0.082 Å with 4-31G) are, nevertheless, particularly striking. The very long C-H bonds in the multiply charged C<sub>5</sub>H<sub>5</sub><sup>3+</sup> and C<sub>6</sub>H<sub>6</sub><sup>4+</sup> cations probably reflect their instability.

For the 6π-electron series, the bond length changes are much more gradual. Even for the multiply charged cations, C<sub>8</sub>H<sub>8</sub><sup>2+</sup> and C<sub>9</sub>H<sub>9</sub><sup>3+</sup>, the predicted carbon-carbon bond lengths are only 0.028 and 0.049 Å, respectively, greater than in benzene. The C-H lengths also do not rise to unreasonable values, even for the trication.

**Molecular Symmetries.** All the results described to this point refer to *n*-carbon systems with assumed *D<sub>nh</sub>* symmetry. Two of the ions were examined, in addition, with lower symmetry to see whether alternation of ring bond lengths is energetically favorable. Thus, calculations were carried out on the cyclobutadiene dication and cyclooctatetraene dication with *D<sub>2h</sub>* and *D<sub>4h</sub>* symmetry assumed for the respective rings. Bond

**Table IV.** Calculated Binding Energies (kcal mol<sup>-1</sup>)

Species	Fragments	Binding energy		
		STO-3G/ STO-3G	4-31G/ STO-3G	4-31G/ 4-31G
C <sub>4</sub> H <sub>4</sub> <sup>2+</sup>	C <sub>3</sub> H <sub>3</sub> <sup>+</sup> + CH <sup>+</sup>	3	1	1
C <sub>5</sub> H <sub>5</sub> <sup>3+</sup>	C <sub>4</sub> H <sub>4</sub> <sup>2+</sup> + CH <sup>+</sup>	-129	-120	
C <sub>6</sub> H <sub>6</sub> <sup>4+</sup>	C <sub>5</sub> H <sub>5</sub> <sup>3+</sup> + CH <sup>+</sup>	-250	-247	
C <sub>7</sub> H <sub>7</sub> <sup>+</sup>	C <sub>6</sub> H <sub>6</sub> + CH <sup>+</sup>	201	189	
C <sub>8</sub> H <sub>8</sub> <sup>2+</sup>	C <sub>7</sub> H <sub>7</sub> <sup>+</sup> + CH <sup>+</sup>	31		
C <sub>9</sub> H <sub>9</sub> <sup>3+</sup>	C <sub>8</sub> H <sub>8</sub> <sup>2+</sup> + CH <sup>+</sup>	-96		

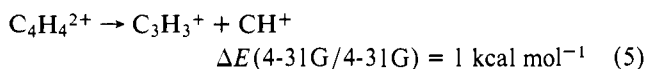
lengths and bond angles to the hydrogen atoms were taken equal to the values in the optimized structures with full symmetry. In both cases, the best structure was found to correspond to equal rather than alternating bond lengths.

**Molecular Energetics.** The present theory may be used to determine the stability of these cations only with respect to fragment systems with the same overall charge. We have initially chosen as fragments the next lowest member of the series together with a CH<sup>+</sup> ion yielding the binding energies shown in Table IV. The good agreement between the three levels of theory for the smaller systems lends strength to the STO-3G/STO-3G predications for the larger systems where more accurate calculations are not possible with our current resources.

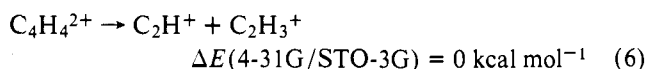
We note that this choice of fragments does not necessarily correspond to the one of lowest energy. For example, for C<sub>4</sub>H<sub>4</sub><sup>2+</sup>, values of 4-31G/STO-3G energies<sup>14a,15a</sup> for a variety of pairs of fragments suggest that fragment systems of lower theoretical energy than C<sub>3</sub>H<sub>3</sub><sup>+</sup> + CH<sup>+</sup> (the pair chosen in our scheme) include C<sub>3</sub>H<sup>+</sup> + CH<sub>3</sub><sup>+</sup> and C<sub>2</sub>H<sub>2</sub><sup>+</sup> + C<sub>2</sub>H<sub>2</sub><sup>+</sup>, although in the latter case and in other systems involving open shells, it must be remembered that the calculations are biased in their favor. Despite the possibility of lower energy fragments in some cases, we have chosen to calculate binding energies as described above to facilitate internal comparisons.

Of the 2π-electron cations, C<sub>4</sub>H<sub>4</sub><sup>2+</sup> is marginally bound on this basis while both C<sub>5</sub>H<sub>5</sub><sup>3+</sup> and C<sub>6</sub>H<sub>6</sub><sup>4+</sup> are strongly unbound. Of the 6π-electron cations, C<sub>7</sub>H<sub>7</sub><sup>+</sup> is very strongly bound, C<sub>8</sub>H<sub>8</sub><sup>2+</sup> moderately bound, and C<sub>9</sub>H<sub>9</sub><sup>3+</sup> quite strongly unbound. These results are in qualitative agreement with the experimental observation of unsubstituted C<sub>7</sub>H<sub>7</sub><sup>+</sup> and of derivatives of C<sub>4</sub>H<sub>4</sub><sup>2+</sup> and C<sub>8</sub>H<sub>8</sub><sup>2+</sup>.

An alternative and more direct means of assessing the thermodynamic stabilities of the polycations is to calculate their heats of formation. These may then be compared with appropriate experimental values for fragment systems. The technique we have employed to estimate the heats of reaction is to utilize the *theoretical* energy change for a fragmentation reaction together with *experimental* (or, in some cases, our calculated) heats of formation for fragment systems. For example, for the cyclobutadiene dication, C<sub>4</sub>H<sub>4</sub><sup>2+</sup>, we use the theoretical (4-31G/4-31G) energy change in reaction 5



together with experimental heats of formation for C<sub>3</sub>H<sub>3</sub><sup>+</sup> (256 kcal mol<sup>-1</sup>)<sup>23</sup> and CH<sup>+</sup> (399 kcal mol<sup>-1</sup>).<sup>24</sup> This yields Δ*H*<sub>f</sub><sup>°</sup> (C<sub>4</sub>H<sub>4</sub><sup>2+</sup>) = 654 kcal mol<sup>-1</sup>. Alternatively, we may use reaction 6



and experimental heats of formation for C<sub>2</sub>H<sup>+</sup> (399 kcal mol<sup>-1</sup>)<sup>24</sup> and C<sub>2</sub>H<sub>3</sub><sup>+</sup> (269 kcal mol<sup>-1</sup>)<sup>25</sup> yielding Δ*H*<sub>f</sub><sup>°</sup> (C<sub>4</sub>H<sub>4</sub><sup>2+</sup>) = 665 kcal mol<sup>-1</sup>. Since calculations with small

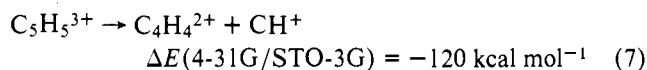
**Table V.** Calculated Heats of Formation (kcal mol<sup>-1</sup>) for Polycations

Cation	Δ <i>H</i> <sub>f</sub> <sup>°</sup>	Cation	Δ <i>H</i> <sub>f</sub> <sup>°</sup>
C <sub>4</sub> H <sub>4</sub> <sup>2+</sup>	660	C <sub>8</sub> H <sub>8</sub> <sup>2+</sup>	580
C <sub>5</sub> H <sub>5</sub> <sup>3+</sup>	1179	C <sub>9</sub> H <sub>9</sub> <sup>3+</sup>	1075
C <sub>6</sub> H <sub>6</sub> <sup>4+</sup>	1825		

basis sets are known to overestimate the energy of strained rings.<sup>14,26</sup> the theoretical energy change for reaction 5 is likely to be too positive, and for reaction 6, not positive enough. We have therefore taken the mean of our two estimates of the heat of formation for the cyclobutadiene dication, i.e., 660 kcal mol<sup>-1</sup>, and this is the value included in Table V.

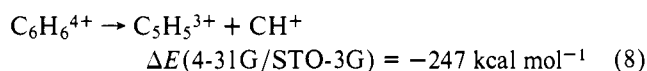
The only combination of fragment ions of C<sub>4</sub>H<sub>4</sub><sup>2+</sup> for which "reliable"<sup>27</sup> experimental heats of formation are available and which have lower energy than this value are C<sub>2</sub>H<sub>2</sub><sup>+</sup> + C<sub>2</sub>H<sub>2</sub><sup>+</sup> and C<sub>3</sub>H<sub>3</sub><sup>+</sup> + CH<sup>+</sup>. The experimental heats of formation suggest that these pairs are respectively 26 and 5 kcal mol<sup>-1</sup> lower in energy than C<sub>4</sub>H<sub>4</sub><sup>2+</sup>. Thus the cyclobutadiene dication is likely to be thermodynamically less stable than these pairs of fragments; the possibility of observation of C<sub>4</sub>H<sub>4</sub><sup>2+</sup> will depend on activation energies for the fragmentation reactions. We have not considered this aspect in detail in this study but make some brief comments later in the paper from the viewpoint of orbital symmetry.

For C<sub>5</sub>H<sub>5</sub><sup>3+</sup>, we can use the theoretical energy change for reaction 7



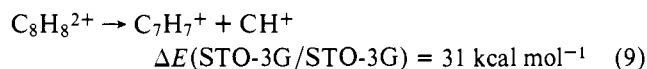
together with the experimental heats of formation for CH<sup>+</sup> and the calculated value (Table V) for C<sub>4</sub>H<sub>4</sub><sup>2+</sup>. This leads to Δ*H*<sub>f</sub><sup>°</sup> (C<sub>5</sub>H<sub>5</sub><sup>3+</sup>) = 1179 kcal mol<sup>-1</sup>. There are several fragment combinations of substantially lower (e.g., by 150 kcal mol<sup>-1</sup>) energy than this and it seems unlikely that C<sub>5</sub>H<sub>5</sub><sup>3+</sup> will be an observable species.

The heat of formation for C<sub>6</sub>H<sub>6</sub><sup>4+</sup> (1825 kcal mol<sup>-1</sup>) was derived from reaction 8.



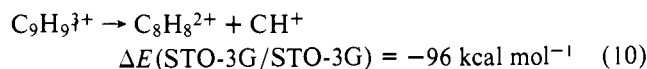
This is clearly an extremely high value and there are many fragment combinations with much lower energy.

For C<sub>8</sub>H<sub>8</sub><sup>2+</sup>, we have used the theoretical energy change in reaction 9



together with experimental Δ*H*<sub>f</sub><sup>°</sup> values for tropylium cation (212 kcal mol<sup>-1</sup>)<sup>25</sup> and CH<sup>+</sup>. This yields Δ*H*<sub>f</sub><sup>°</sup> (C<sub>8</sub>H<sub>8</sub><sup>2+</sup>) = 580 kcal mol<sup>-1</sup>. Fragments of lower energy include C<sub>6</sub>H<sub>6</sub><sup>+</sup> + C<sub>2</sub>H<sub>2</sub><sup>+</sup> (lower by 30 kcal mol<sup>-1</sup>), C<sub>6</sub>H<sub>5</sub><sup>+</sup> + C<sub>2</sub>H<sub>3</sub><sup>+</sup> (29 kcal mol<sup>-1</sup>), and C<sub>3</sub>H<sub>3</sub><sup>+</sup> + C<sub>3</sub>H<sub>3</sub><sup>+</sup> + C<sub>2</sub>H<sub>2</sub> (14 kcal mol<sup>-1</sup>). As for C<sub>4</sub>H<sub>4</sub><sup>2+</sup>, the possibility for observing C<sub>8</sub>H<sub>8</sub><sup>2+</sup> will depend on the activation energy for these exothermic fragmentation reactions.

Finally, for C<sub>9</sub>H<sub>9</sub><sup>3+</sup>, we use reaction 10

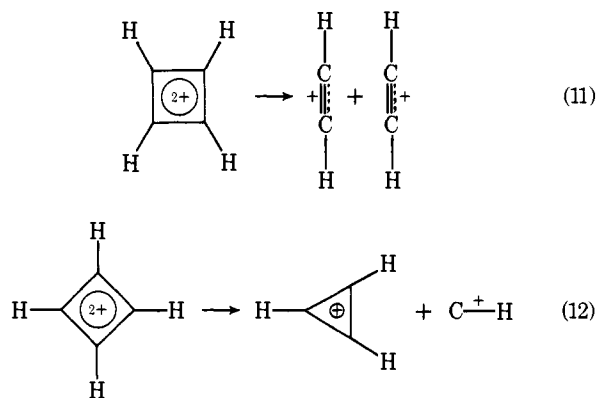


to obtain Δ*H*<sub>f</sub><sup>°</sup> (C<sub>9</sub>H<sub>9</sub><sup>3+</sup>) = 1075 kcal mol<sup>-1</sup>. This is higher in energy than three cyclopropenyl cations by greater than 300 kcal mol<sup>-1</sup>. It would seem most unlikely that the (unsubstituted) C<sub>9</sub>H<sub>9</sub><sup>3+</sup> trication will be observable.

A possibility which we have not yet explored in detail is ring opening to an open-chain polycation. However, trial calcula-

tions on structures derived by hydride abstraction from each terminus of planar 1,3-butadiene (giving  $C_4H_4^{2+}$ ) and 1,3,5,7-octatetraene (giving  $C_8H_8^{2+}$ ) yield higher energies than for the corresponding cyclic isomers.

The arguments above refer, of course, to *thermodynamic* stability. In practice, the stability of the cations will also depend on the activation energy for possible rearrangement or fragmentation reactions, i.e., the *kinetic* stability. For  $C_4H_4^{2+}$ , for example, the most likely fragmentation reactions are 11 and 12. The least motion paths for both of these processes are



“forbidden” from the point of view of orbital symmetry considerations and are therefore likely to require significant activation energy. For reaction 11, the pertinent observation is that the two unpaired electrons of the  $C_2H_2^+$  fragments will come from the  $\pi$  system of the cyclobutadiene ring. The four  $\pi$  electrons of the orthogonal  $\pi$  system of the  $C_2H_2^+$  ions can be considered to arise from a coplanar cycloreversion, directly analogous to the cyclobutane  $\rightarrow$  2(ethylene) reaction which is symmetry forbidden.<sup>28</sup> Reaction 12 under  $C_{2v}$  symmetry involves a change in electronic configuration from  $a_1^{16}b_1^8b_2^2$  to  $a_1^{18}b_1^6b_2^2$ , and is again symmetry forbidden. Thus, although  $C_4H_4^{2+}$  may be thermodynamically less stable than some of its fragmentation products, it is possible that it will be observable in the laboratory because of large activation barriers for reactions such as 11 and 12. We note that reactions analogous to 12 for the higher polycations, e.g.,  $C_9H_9^{3+} \rightarrow C_8H_8^{2+} + CH^+$ , are also symmetry forbidden.

**Methyl Derivatives.** Prompted by the experimental observation of the tetramethylcyclobutadiene dication, we have carried out additional calculations on this species and appropriate fragments giving the results shown in Table VI. We can see that methyl substitution leads to increased binding energy. It is therefore not unexpected that observation of the unsubstituted cyclobutadiene dication has presented greater experimental difficulty than has the tetramethyl derivative. More refined calculations on the tetramethylcyclobutadiene dication in which the ring carbon-carbon bond lengths were also optimized showed that the ring structure is unaffected by the methyl substituent. Thus the optimum STO-3G structure for the tetramethylcyclobutadiene dication has the ring C-C = 1.467 Å and the methyl C-C = 1.505 Å. Taking into account both our STO-3G and 4-31G results for the cyclopropenyl cation and cyclobutadiene dication, we would expect the ring C-C distance in the tetramethylcyclobutadiene dication to lie within the range  $1.455 \pm 0.02$  Å, i.e., 0.08–0.09 Å longer than the experimental bond lengths in cyclopropenyl cation derivatives.

## Conclusions

The following points emerge from this ab initio molecular orbital study of the  $2\pi$ -electron cations  $C_3H_3^+$ ,  $C_4H_4^{2+}$ ,  $C_5H_5^{3+}$ , and  $C_6H_6^{4+}$ , and the  $6\pi$ -electron systems,  $C_6H_6$ ,  $C_7H_7^+$ ,  $C_8H_8^{2+}$  and  $C_9H_9^{3+}$ .

**Table VI.** Theoretical Data (STO-3G) for Methylated Derivatives

	$C(CH_3)^+$	$C_3(CH_3)_3^+$	$C_4(CH_3)_4^{2+}$
C-C, Å	1.463	1.505	1.505
Energy, hartrees	-76.12147	-229.44309	-305.58238
Binding energy, kcal mol <sup>-1</sup>			11.2

(1) A convenient approximate guide to stability is provided by binding energies with respect to the next lowest member of each series plus  $CH^+$ . On this basis, the monocation  $C_7H_7^+$  is predicted to be strongly bound, the dications  $C_4H_4^{2+}$  and  $C_8H_8^{2+}$  weakly bound, the trications  $C_5H_5^{3+}$  and  $C_9H_9^{3+}$  unbound, and the tetracation  $C_6H_6^{4+}$  very strongly unbound. In each case, the  $6\pi$ -electron cation is more strongly bound (or less unbound) than the corresponding  $2\pi$ -electron system.

(2) These predictions correlate directly with the nature of the occupied and unoccupied orbitals in the Hückel approximation.

(3) Similar conclusions are reached from comparisons of calculated heats of formation for the polycations with experimental values for a variety of possible fragment systems. For the dications  $C_4H_4^{2+}$  and  $C_8H_8^{2+}$ , there are fragments about 30 kcal mol<sup>-1</sup> lower in energy and the possibility of observation of these ions will depend on the activation energy for the fragmentation reactions. For  $C_5H_5^{3+}$ ,  $C_9H_9^{3+}$ , and  $C_6H_6^{4+}$ , it is found that fragment systems exist with substantially (>150 kcal mol<sup>-1</sup>) lower energy. It seems highly unlikely that these ions will be observable.

(4) Carbon-carbon bond lengths in the  $2\pi$ -electron ions increase quite rapidly in moving from  $C_3H_3^+$  to  $C_6H_6^{4+}$ . The increase in lengths in the  $6\pi$ -electron systems is much more gradual.

(5) The  $C_4H_4^{2+}$  and  $C_8H_8^{2+}$  dications are each predicted to have equal rather than alternating C-C bond lengths.

(6) Tetramethyl substitution in  $C_4H_4^{2+}$  giving rise to the experimentally observed  $C_4(CH_3)_4^{2+}$  dication is predicted to lead to an increase in binding energy.

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## Heats of Formation of Some Isomeric $[C_nH_{2n+1}O]^+$ Ions. Substitutional Effects on Ion Stability

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**Abstract:** Heats of formation for a number of isomeric ions of formula  $[CH_3O]^+$ ,  $[C_2H_5O]^+$ ,  $[C_3H_7O]^+$ ,  $[C_4H_9O]^+$ , and  $[C_5H_{11}O]^+$  have been measured by monoenergetic electron impact. The stabilization brought about by substituting methyl groups on the C and O atoms in these ionic species is compared with that found in their alkyl ion counterparts. The question of the localization of charge in such species is discussed.

In recent papers of this series<sup>1,2</sup> the heats of formation of a variety of isomeric hydrocarbon positive ions have been reported. In these experiments free radicals of known structure, generated by flash thermolysis at pressures of around  $10^{-3}$  Torr, were bombarded by a monochromatic electron beam. With sufficient experimental sensitivity and appropriate calibration of the energy scale<sup>3</sup> the ionization onset is generally found to be lower than the vertical ionization potential and may approximate to the adiabatic ionization potential. Provided that radicals of the desired structure can be produced by thermolysis and that the heats of formation of the neutral radicals are known or can be estimated sufficiently closely, this method can yield heats of formation of different isomeric ions of the same composition. This is particularly valuable in the situation, frequent for the less stable isomers of hydrocarbon ions, where dissociative ionization thresholds (appearance potentials) correspond to rearrangements to one of the more stable isomers and not to the ion expected on the basis of simple bond rupture.<sup>1,4</sup>

Attempts in this laboratory to obtain ionic heats of formation for isomers of oxygen-containing carbocations (oxycarbonium ions) by this method have been frustrated by the difficulties of producing the corresponding oxygenated free radicals in sufficient yields by flash thermolysis. Only two of these radicals,  $CH_3OCH_2$  and  $CH_3CHOCH_3$ , have been produced so far in acceptable yields. It is therefore necessary at present to rely on dissociative ionization thresholds. The lower reliability of such measurements, resulting from the possibility of ionic rearrangements, is perhaps less serious for these ions than for hydrocarbon ions. There is considerable evidence that at low energy contents oxycarbonium ions rearrange much less freely than do hydrocarbon ions. McLafferty and Sakai<sup>5</sup> have concluded that the evidence from metastable ion spectra<sup>6</sup> and particularly from collisional activation spectra<sup>5</sup> shows that the four structures of formula

$[C_3H_7O]^+$  discussed in the present work are stable ion structures. Ion cyclotron<sup>7</sup> and collisional activation<sup>8</sup> studies have identified the two  $[C_2H_5O]^+$  structures discussed below as stable species, noninterconverting at low energy contents. By careful choice of dissociation processes, that is, by selecting a parent molecule from which the desired ion can be made by the minimum-energy, single-bond rupture process, the possibility of rearrangements has been minimized in the present work. The choice of such processes is also desirable for minimizing uncertainties resulting from the kinetic shift and reverse activation energies.<sup>9</sup>

A number of earlier studies of the energetics of  $[CH_3O]^+$ ,  $[C_2H_5O]^+$ ,  $[C_3H_7O]^+$ , and  $[C_4H_9O]^+$  ions have been published. The most recent data are those of Haney and Franklin<sup>10</sup> using RPD electron impact, and of Refaey and Chupka<sup>11</sup> and of Botter, Pechine, and Rosenstock<sup>12</sup> using photon impact. Earlier results, using conventional ion sources, are reported in the NBS compilation.<sup>13</sup> The emphasis in the present work is directed toward obtaining a consistent scheme for the heats of formation of isomeric oxycarbonium ions rather than toward interpreting the dissociation mechanisms of their precursors.

Some of the ions investigated here, those containing -OH groups, are identical with the structures formed by proton transfer to aldehydes and ketones; for these, ionic heats of formation are in some cases available from gas-phase ionic equilibria. As will be seen below, the results of this investigation are in satisfactory agreement with current data of this origin. For the ions containing C-O-C linkages, however, such data are not available.

### Experimental Section

Ionization efficiency and appearance potential curves were obtained as described previously, using an electrostatic electron monochromator coupled to a quadrupole mass filter.<sup>14</sup> The initial portions of the curves