Gaseous Ions. 1. MINDO/3 Study of the Rearrangement of Benzyl Cation to Tropylium

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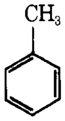
Abstract: The mechanism of the rearrangement of benzyl cation into tropylium seems to have been established by MINDO/3 calculations. The reaction involves several stable intermediates and the calculated overall activation energy is 32.7 kcal/mol. The rearrangements of *o*-, *m*-, and *p*-tolyl cations to benzyl cation or tropylium have been studied.

It has been known for some time[1a,b] that the mass spectra of a number of C_7H_8 hydrocarbons, in particular toluene (**1**) and cycloheptatriene (**2**), exhibit strong peaks at *m/e* 91 ($C_7H_7^+$), and the same has been shown to be the case for a number of their derivatives C_7H_7X.[1] The similarity of the observed fragmentation patterns moreover suggested that the $C_7H_7^+$ species was the same in all cases and isotopic labeling experiments[1a,b,2a-d] have indicated that complete scrambling of both carbon and hydrogen occurs during its formation, at least in the case of $C_7H_7^+$ ions, with enough excess energy to undergo fragmentation. While it seems very likely that this common ion is tropylium (**3**), the ways in which it is formed from the various precursors, and the mechanisms of the scrambling processes, remain uncertain.[1]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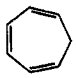
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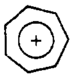
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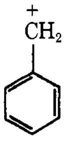
The formation of **3** from **1** could take place by rearrangement of benzyl cation (**4**), formed from the toluene molecular ion (**5**) by loss of a hydrogen atom.[1b,2e,f] The experimental evidence indicates that conversion of **4** to **3** should be exothermic by 7 kcal/mol.[3] Alternatively, **5** might first rearrange to cycloheptatriene molecular ion (**6**) which could in turn yield **3** by loss of hydrogen. If the conversion of **5** to **6** were rapid and reversible, this could account for the observed isotopic scrambling. Since various reasonable mechanisms can be written for the various interconversions, a large number of possibilities have to be considered.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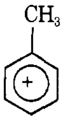
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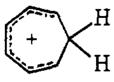
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Problems such as this are much more difficult to resolve by experimental methods than those arising from "normal" chemical reactions. For example, isomers can as a rule be distinguished only by their fragmentation patterns and these apply only to ions with enough excess vibronic energy to fragment. It cannot be assumed that less energetic ions will behave likewise. A further problem is the difficulty of measuring rates of reactions. At present, the most that can be done is to establish a qualitative order for the rates of reactions of a given ion and perhaps set limits to their possible activation energies. Given the difficulty of establishing even the reactions that take place in a mass spectrometer, attempts to determine their mechanisms by experiment can hardly lead to unequivocal conclusions.

The area of mass spectral reactions is therefore one where theoretical calculations could be of especial value, in particular using the MINDO/3 semiempirical SCF method.[4] MINDO/3 is now established[5] as a powerful procedure for the study of reaction mechanisms; while most of the work hitherto has been concerned with nonionic reactions, there is no reason to suppose that it will be any less effective for ionic ones. Calculations have indicated that MINDO/3 is equally applicable to ions and neutral molecules and preliminary calculations for several ionic reactions have given good results.

We therefore decided to carry out a detailed MINDO/3 study of the $C_7H_7^+$ and $C_7H_8^{+\cdot}$ potential surfaces, partly in the hope that the results might be of value in interpreting the mass spectral data and partly as a check on the potential of MINDO/3 in such connections, for this problem has been studied very effectively and in a very intensive manner, notably by McLafferty and his collaborators.[6]

The potential surfaces turned out to be unusually complicated and the resulting mechanistic possibilities correspondingly rich. Indeed, the $C_7H_8^{+\cdot}$ system is by far the most complicated one yet studied by MINDO/3. It seemed to us better to describe the results for the two systems separately, partly because they could not all be reported in a single paper of reasonable length, and partly because the possible interconversion of ions such as **3** and **4** has obvious implications in other areas of chemistry.

Here we report our results for the $C_7H_7^+$ system. Those for $C_7H_8^{+\cdot}$ will be given in the following paper, together with a general discussion of the results of both sets of calculations in relation to the available mass spectral data.

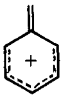
Procedure

The calculations were carried out by the standard MINDO/3 procedure[4] together with the associated DFP geometry program.[4] The calculations for the $C_7H_8^{+\cdot}$ species were carried out by a MINDO/3 program[7] based on the unrestricted Hartree-Fock (UHF) method, rather then the "half-electron" method,[8] because the DFP geometry optimization program operates much more effectively using the UHF procedure. In the "half-electron" method problems arise in the calculation of derivatives of the energy, due to the fact that the bond order matrix is not invariant for small changes in the geometry. These difficulties are avoided in the UHF treatment. Minimum energy reaction paths (MERP) were determined by the usual reaction coordinate method,[9] the energy being minimized with respect to all other geometrical variables for successive increments in the reaction coordinate. The transition states, located approximately from the MERP's, were refined by minimizing the scalar gradient.[10] It was established that each such structure was a true transition state by diagonalizing the force constant matrix and thus determining that it had one, and only one, negative eigenvalue.[10]

Results and Discussion

The geometries, heats of formation, and distributions of formal charge calculated for **3** and **4** are shown in Figure 1.

Curiously enough, no structural data for **3** have been reported, although stable crystalline tropylium salts have been available for 20 years. As one would expect, the ring has D_{7h} symmetry with "aromatic" CC bond lengths (1.405 Å).[11] The geometry calculated for **4** is interesting, corresponding most closely to the classical structure **7**. Here the lack of experimental data is less surprising since **4** is known only in solution or in the gas phase.



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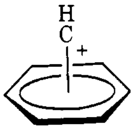

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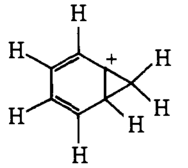

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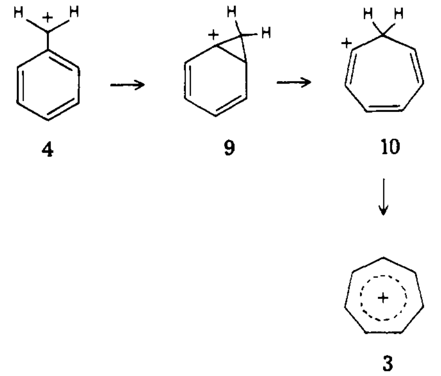
Our calculated heat of formation for **4** (220.4 kcal/mol) agrees well with experiment (216 kcal/mol[3]), but the calculated value for **3** (195.6 kcal/mol) is a good deal less than the reported experimental one (209 kcal/mol[3]). The latter was, however, derived from a spectroscopic value for the ionization potential of tropyl radical. Since the extra electron in tropyl is antibonding, the geometry is likely to differ greatly from that of **3**. Part of the discrepancy could then be due to a large difference between the vertical and adiabatic ionization potentials, the "experimental" heat of formation being correspondingly high. This point will be discussed in detail in the following paper, in connection with a similar but even larger discrepancy for the cycloheptatriene molecular ion (**6**).

Figure 1 also shows the results of calculations for a third $C_7H_7^+$ structure, one (**8**) with C_{6v} symmetry, which Rinehart et al.[2c,12] have postulated as a possible intermediate to explain the observed scrambling of carbon atoms. We found **8** not to be a minimum on the MINDO/3 potential surface. In order to calculate it, we had to enforce C_{6v} symmetry. Our value for the heat of formation is very high indeed, suggesting that **8** is unlikely to be involved in the manner suggested by Rinehart et al.[2c,12] Moreover the mechanisms considered below provide a much more facile route for carbon scrambling.

Our studies suggest that the easiest path from benzyl cation (**4**) to tropylium (**3**) is that indicated in Scheme I, a three-step process involving as stable intermediates the norcaradienyl cation (**9**) and the 1-cycloheptatrienyl cation (**10**). The structures of these intermediates, together with their heats of formation and the distributions of formal charge in them, are shown in Figure 2 while Figure 3 lists comparable data for the various transition states.

Scheme I



The first step involves an addition of the methylene group in **4** across an adjacent bond in the ring. We studied all possible deformations of **4** and are therefore certain that this represents

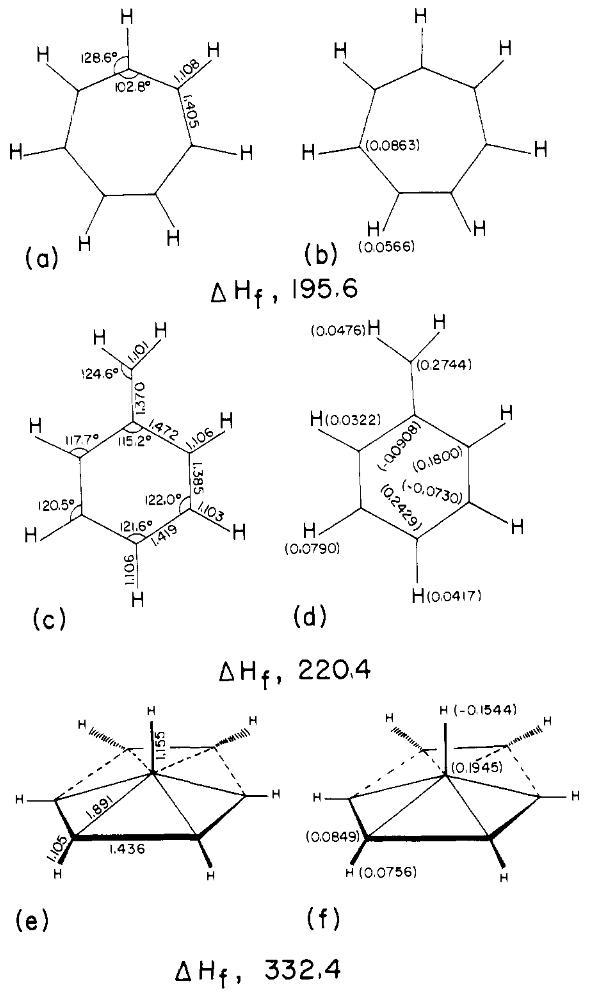


Figure 1. Calculated geometries, heats of formation (ΔH_f, kcal/mol at 25 °C), and distributions of formal charge: (a) (b) for **3**; (c) (d) for **4**; (e) (f) for **8**.

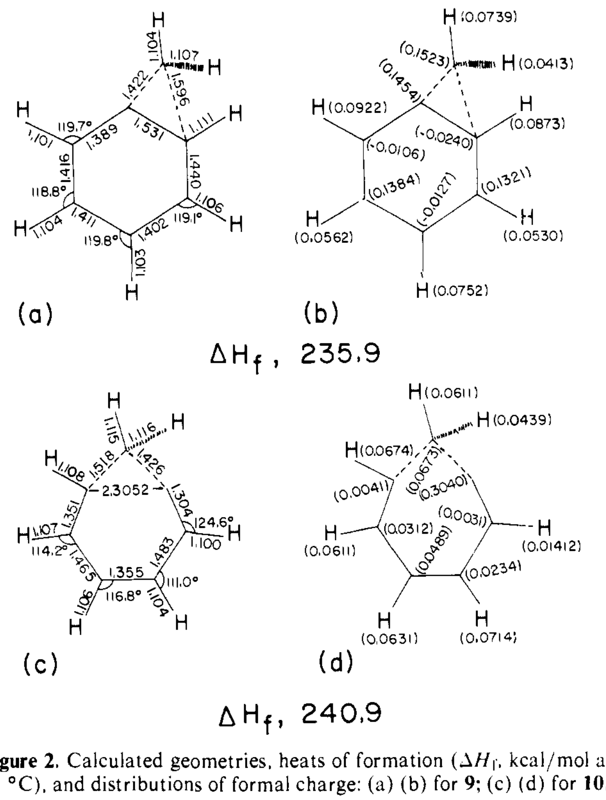


Figure 2. Calculated geometries, heats of formation (ΔH_f, kcal/mol at 25 °C), and distributions of formal charge: (a) (b) for **9**; (c) (d) for **10**.

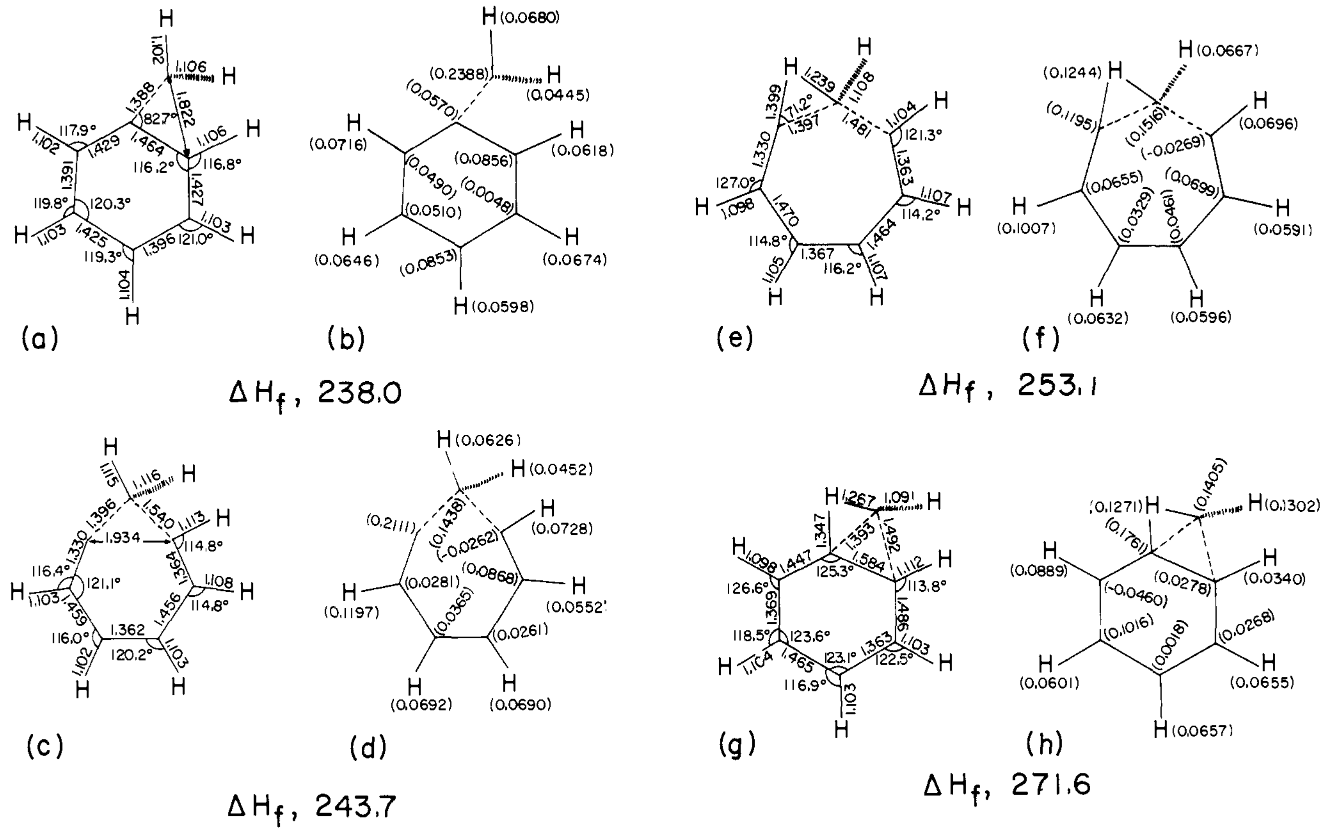
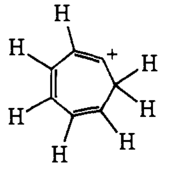


Figure 3. Calculated geometries, heats of formation (ΔH_f, kcal/mol at 25 °C), and distributions of formal charge in the transition states: (a) (b) for **4** → **9**; (c) (d) for **9** → **10**; (e) (f) for **10** → **3**; (g) (h) for **9** → **22**.

the easiest process leading to a bond between the exocyclic carbon atom and a carbon atom in the ring. The resulting adduct **9** differs from norcaradiene in the way one would expect, the positive charge being delocalized over five carbon atoms (see **11**) and the CC bonds in this C_5 unit consequently being similar in length (1.402 ± 0.014 Å). A further interesting point is the large difference between the lengths of the two CH_2–C bonds, 1.422 and 1.596 Å. One of them is presumably shortened by hyperconjugation between the methylene group and the adjacent C_5^+ moiety.

The next step involves fission of the bond common to the two rings in **9** to form **10**, a process analogous to the well-known interconversion of norcaradienes and cycloheptatrienes. Our calculated activation energy for **9** → **10** (7.8 kcal/mol) is indeed similar to the values reported for conversion of 7-cyano-7-trifluoromethylnorcaradiene (**12a**) to 7-cyano-7-trifluoromethylcycloheptatriene (**13a**) (6.7 kcal/mol[13]) and of dimethyl norcaradiene-7,7-dicarboxylate (**12b**) to dimethyl cycloheptatriene-7,7-dicarboxylate (**13b**) (7 kcal/mol[14,15]).



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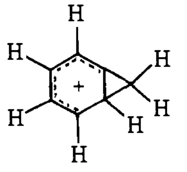

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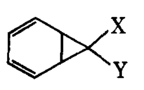
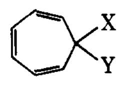
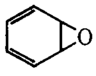


12a, X = CN; Y = CF_3
b, X = Y = $COOCH_3$



13a, X = CN; Y = CF_3
b, X = Y = $COOCH_3$



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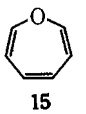

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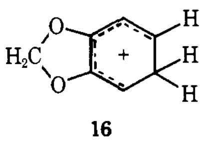

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Moreover the calculated (MINDO/3) barrier for the analogous conversion of **14** to **15** (12.5 kcal/mol[16]) is in reasonable agreement with experiment (9.1 ± 0.8 kcal/mol[17]).

Our calculations indicate that **10** is well represented by the indicated classical structure, being thus a vinyl cation with localized bonds and charge. Vinyl cations are now well established as reaction intermediates[18] and such species have recently been detected in solution by low-temperature NMR spectroscopy.[19]

There is the possibility that **10** might in fact have a triplet ground state, as has been suggested for the analogous phenyl cation. We have not studied this possibility since it would not affect our conclusions concerning the overall conversion of **4** to **3**.

The last step involves a 1,2-hydrogen shift, a very familiar process. Although there seem to be no precise analogies for the present case, one might expect it be similar to the 1,2 migration of hydrogen in a benzenonium ion. Our calculated activation energy (12.2 kcal/mol) is indeed similar to those values reported by Brouwer et al.[20] for the conversions of **16** to **17** (>12 kcal/mol) and of **18** to **19** (11.3 kcal/mol).

All the steps in our scheme therefore seem reasonable. Indeed, they exactly parallel the mechanism suggested by Crow and Paddon-Row[21] for the analogous conversion of phenylcarbene (**20**) to cycloheptatrienecarbene (**21**).

The only other reasonable path from **9** to **10** seems to be one in which the hydrogen shift precedes ring opening, via the 7-norcaradienyl cation (**22**). We studied this path in detail and the structure of the corresponding transition state is also shown in Figure 3. As might be expected, **22** proved unstable, undergoing ring opening to tropylium without activation. However, the energy of the transition state for this one-step conversion of **22** to **3** was found to be very high, greater by 18.5 kcal/mol than that via **9** and **10**. We therefore think that the latter route is much more probable.

Our conclusions are summarized in Figure 4, which shows the energy profile along the MERP for **4** → **9** → **10** → **3**. The overall activation energy is 32.7 kcal/mol. The mass spectral evidence,[22] and studies by ion cyclotron resonance spectros-

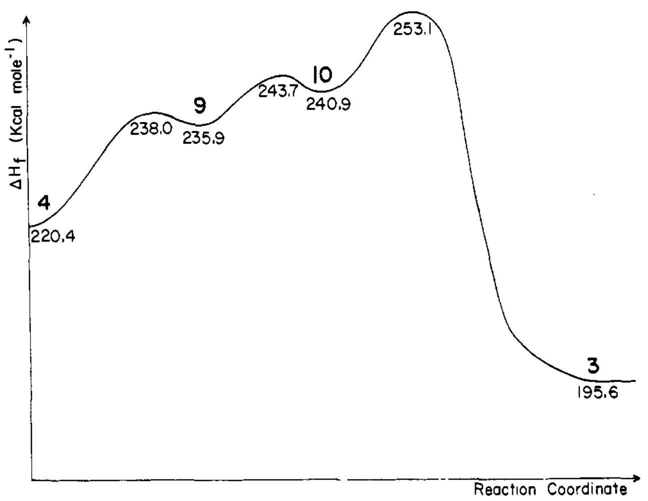
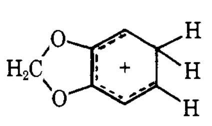


Figure 4. Calculated MERP for **4** → **9** → **10** → **3**.



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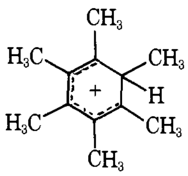

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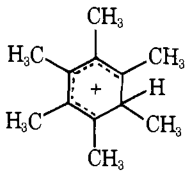

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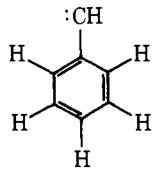

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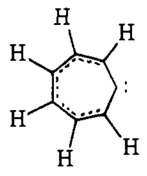

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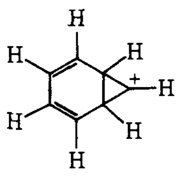

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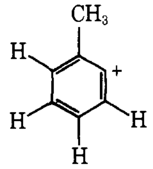

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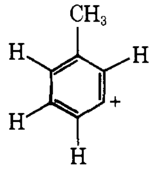

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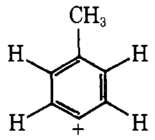

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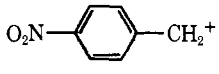
copy,[23] indicate that the ions are separated by an appreciable activation barrier but lead to no estimate of its size. Our value is low enough to be consistent with the mass spectral evidence since ions with enough energy to fragment would certainly have enough to rearrange. It should be added that our estimate of the activation energy is probably somewhat too low, given that MINDO/3 seems to overestimate the stability of **3** relative to **4**.

The high barrier makes it extremely unlikely that the rearrangement, **3** → **4**, will ever be observed in solution, particularly since the solvation energy of **3** is likely to be greater than that of **4** (because of the greater delocalization of charge in the latter). The best hope would seem to lie in a negatively para-substituted benzyl cation such as



where the nitro group should exert a stronger destabilizing effect than it does in tropylium. However, it seems to us unlikely that the barrier could be sufficiently reduced in this way.

A related problem is concerned with the possible rearrangement of tolyl cations (**23**-**25**) to **3**, possibly via **4**. Reactions of this kind have been postulated[1b,22,24] to account for the mass spectra of tolyl derivatives $CH_3C_6H_5X$, where X = NO_2, I, $COCH_3$, COC_6H_5, or $COOCH_3$, but there is little concrete evidence concerning the structures of the derived $C_7H_7^+$ ions. We therefore also studied these species and their rearrangements to **3** and **4**.

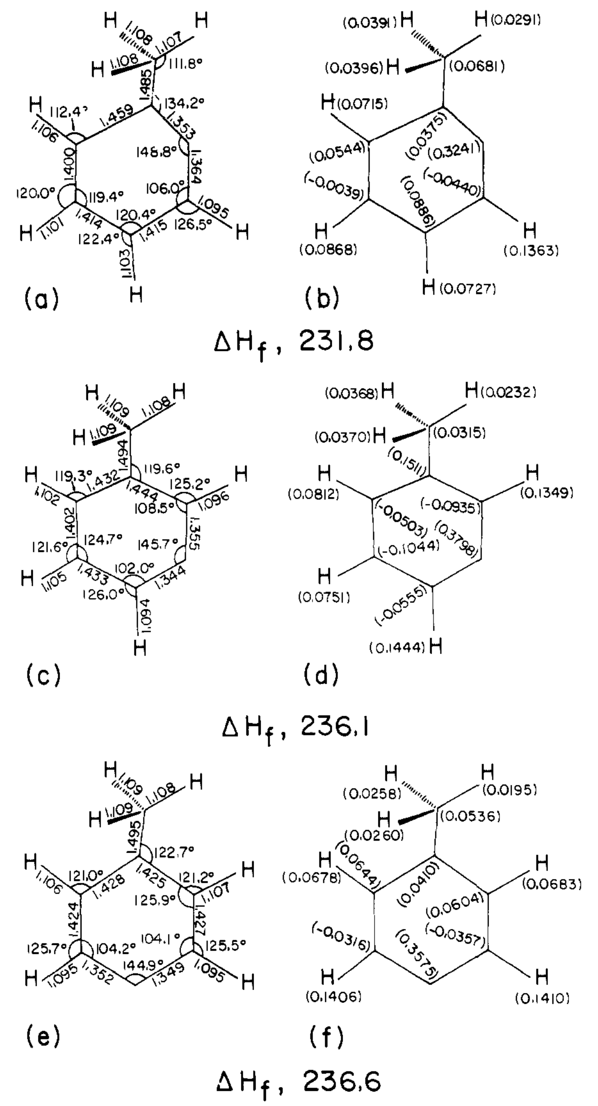


Figure 5. Calculated geometries, heats of formation (ΔH_f, kcal/mol at 25 °C), and distributions of formal charge: (a) (b) for **23**; (c) (d) for **24**; (e) (f) for **25**.

The calculated geometries, heats of formation, and distributions of formal charge in **23**, **24**, and **25** are shown in Figure 5. Since complications can arise in cases where the energy is almost independent of one variable, and since this is almost certainly true for rotation of the methyl group in each of these species, we assumed that one of the methyl hydrogen atoms lies in the plane of the ring.[25]

Figure 6 shows the transition state for rearrangement of *o*-tolyl cation (**23**) to **4**. The calculated activation energy is 25 kcal/mol so this reaction should occur quite easily in the mass spectrometer. Figure 6 also shows the transition state for rearrangement of **24** to **23**. The calculated activation energy (38.9 kcal/mol), while high, is still in the region leading to feasible mass spectral processes. Since moreover the transition state is much higher in energy (by 18.2 kcal/mol) than that for **23** → **4**, it is very likely that **24** would rearrange directly to **4** without being trapped at **23**.

While no calculations seem to have been carried out for edge-protonated structures, such as the transition states in Figure 6, ab initio calculations[26] for protonated acetylene make out results seem quite reasonable. These indicate that the

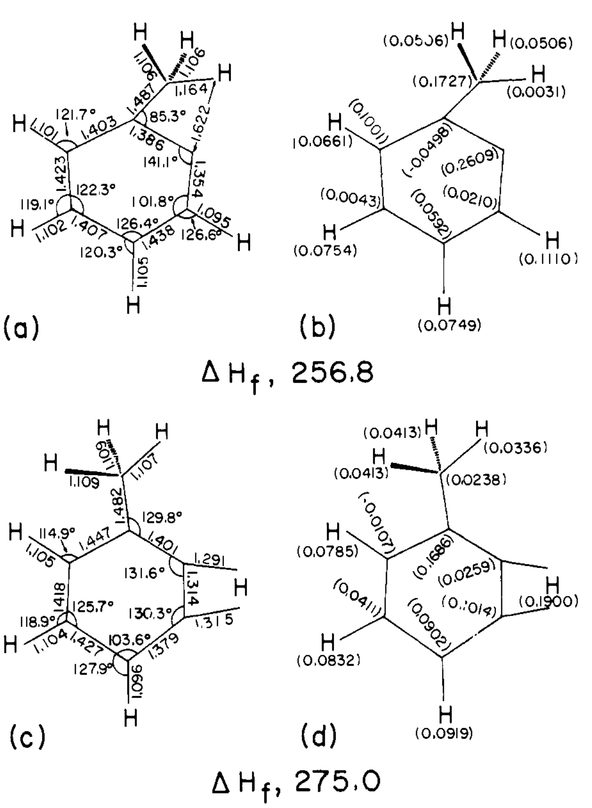


Figure 6. Calculated geometries, heats of formation (ΔH_f, kcal/mol at 25 °C), and distributions of formal charge in the transition states: (a) (b) for **23** → **4**; (c) (d) for **24** → **23**.

bridged structures are less stable than the corresponding vinyl cations by 18-25 kcal/mol, about the same as the difference between the energies calculated for **24** and **23** and for the transition state for their interconversion.

Our calculations therefore seem to be consistent with the view that all the $C_7H_7^+$ ions studied here, other than **8**, can interconvert under the conditions in a mass spectrometer. Since moreover an ion has little chance to lose initial vibrational energy under these conditions, the reactions should be rapidly reversible. If so, attempts to identify the specific species corresponding to the $C_7H_7^+$ peak in an ordinary electron impact mass spectrum are somewhat pointless and the rapid interconversion would of course also lead to complete scrambling of both carbon and hydrogen.

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References and Notes

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