(86) P. W. Dillon, unpublished results.
(87) In this particular study bond lengths were fixed temporarily.
(88) Since "rotation" could eliminate the best point, this is retained and if the best point in the new simplex is not as good we immediately proceed to step 4 and move toward the minimum.
(89) We have found a value of 0.3 kcal/mol yields adequate geometries in a reasonable number of iterations.[86]
(90) This is based upon the fact that near the optimum each partial derivative is close to zero and $R_j - R_1 \approx (\partial R/\partial V_i)(V_{ij} - V_{i1}) \approx 0$ where R is the response function, R_j the response at point j, and V_{ij} is the value of the ith variable at the jth point. In principle there could arise a problem if the $(V_{ij} - V_{i1})$ terms were too small as the result of a large number of rotations in which case the simplex might appear to converge without actually reaching the optimum. We have not had any such difficulty to date however.[86]
(91) A similar expedient was chosen to determine when to expand the simplex and free the temporarily fixed variables. Thus, simplex expansion was performed when the total spread in energies was <1 kcal/mol.
(92) The Univac 1108 version of Fortran IV.
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Gaseous Ions. 2.[1] MINDO/3 Study of the Rearrangements of Toluene and Cycloheptatriene Molecular Ions and the Formation of Tropylium

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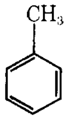
Abstract: Several reaction paths for rearrangement of toluene molecular ion (TMI) to cycloheptatriene molecular ion (CHMI) have been studied, using MINDO/3. The results are in qualitative agreement with experiment and lead to the following conclusions: (a) the activation energy for interchange of ring hydrogen in TMI is less than for methyl-ring exchange; (b) there are several paths from TMI to CHMI with similar overall activation energies; (c) scrambling of hydrogen in CHMI is easier than in TMI: (d) loss of hydrogen from CHMI is easier than from TMI.

The mass spectra of various compounds C_7H_7X, including toluene (**1**) and cycloheptatriene (**2**), show a strong peak at *m/e* 91 ($C_7H_7^+$) which has been attributed to tropylium[2] (**3**). If the starting material is isotopically labeled, the fragmentation patterns observed indicate that extensive scrambling of carbon and hydrogen occurs during formation of **3**.[2-7] In the preceding paper[1] we reported a detailed MINDO/3 study of the conversions of benzyl cation (**4**), and of other tolyl cations, into **3**. Here we report a similar study of the parts of the $C_7H_8^{+\cdot}$ potential surface relevant to the interconversion of toluene molecular ion (TMI, **5**) and cycloheptatriene molecular ion (CHMI, **6**) and their conversions to $C_7H_7^+$ species. As will be seen presently the results are not only consistent with the very extensive experimental data now available but in conjunction with them seem to lead to definite mechanisms for the various processes involved.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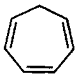
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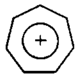
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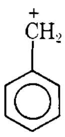
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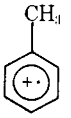
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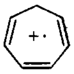
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Procedure

The calculations were carried out using a spin-unrestricted version[8] of MINDO/3[9] together with the associated DFP geometry program.[9] The procedure was otherwise the same as in part 1.[1] All geometries were optimized with respect to all geometrical variables, no assumptions whatsoever being made.

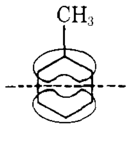
Notation

Reactions are indicated in the text in parentheses, e.g., (**5** → **6**). Transition states are represented likewise, but using square brackets, e.g., [**5** → **6**] would be the transition state for (**5** → **6**).

Results and Discussion

(1) **Properties of 5 and 6.** Figure 1 shows the geometries, heats of formation, and distributions of formal charge calculated for TMI (**5**) and CHMI (**6**).

The heat of formation calculated for **5** (212.2 kcal/mol) agrees very well with experiment (215 kcal/mol[10]). The geometry is interesting, corresponding to a distortion of the ring in the direction of the classical structure **7**. This can be understood very easily in terms of PMO theory[11] by arguments that have already been used to explain[12] the photoelectron spectrum of **1**. The HOMO in benzene consists of a pair of degenerate π MO's. In **1**, the degeneracy is removed by hyperconjugative interaction with methyl, the MO indicated in **7** increasing in energy while that indicated in **8** remains unchanged. Conversion of **1** to **5** therefore involves loss of an electron from the MO of **7**. Now this MO is antibonding between the 2,3 and 5,6 positions in toluene but bonding between the other pairs of adjacent ring atoms. Removing an electron from it should therefore lead to contraction of the 2,3 and 5,6 bonds and lengthening of the others in the ring, i.e., the distortions predicted by our calculations. Likewise the formal positive charge should be concentrated mainly in the 1,4 positions, as our calculations again predict.



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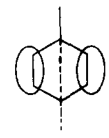

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The heat of formation calculated for **6** (206.6 kcal/mol) was, however, very much lower than the experimental value (240 kcal/mol).[10] It was obvious that this discrepancy had to be resolved if we were to put any trust in MINDO/3 calculations for the $C_7H_8{}^{+\cdot}$ potential surface. The MINDO/3 heat of formation for cycloheptatriene (**2**) itself (37.3 kcal/mol) is in reasonable agreement with experiment (43.9 kcal/mol[13]). The trouble lies in a major discrepancy between the calculated ionization potential of **2** (7.34 eV) and that observed (8.52 eV[10,14,15]).

MINDO/3 ionization potentials can be estimated by two different procedures, either by applying Koopmans' theorem or (as here) by difference between the heats of formation calculated for a molecule and for the corresponding molecular ion. The former should approximate the vertical ionization potential, the latter the adiabatic one. Usually the two values differ by only a few tenths of an electron volt, the vertical being naturally the larger. Here, however, the MINDO/3 value[16] for **2** from Koopman's theorem (8.47 eV) is very much greater than the adiabatic one, being in good agreement with experiment.[10,14,15] This suggests that the discrepancy indicated above could be due to an abnormally large difference between the vertical and adiabatic ionization potentials for **2**, the experimental value corresponding to vertical ionization.

The following argument shows that the latter value must in fact be much greater than the true adiabatic ionization potential of **2**.

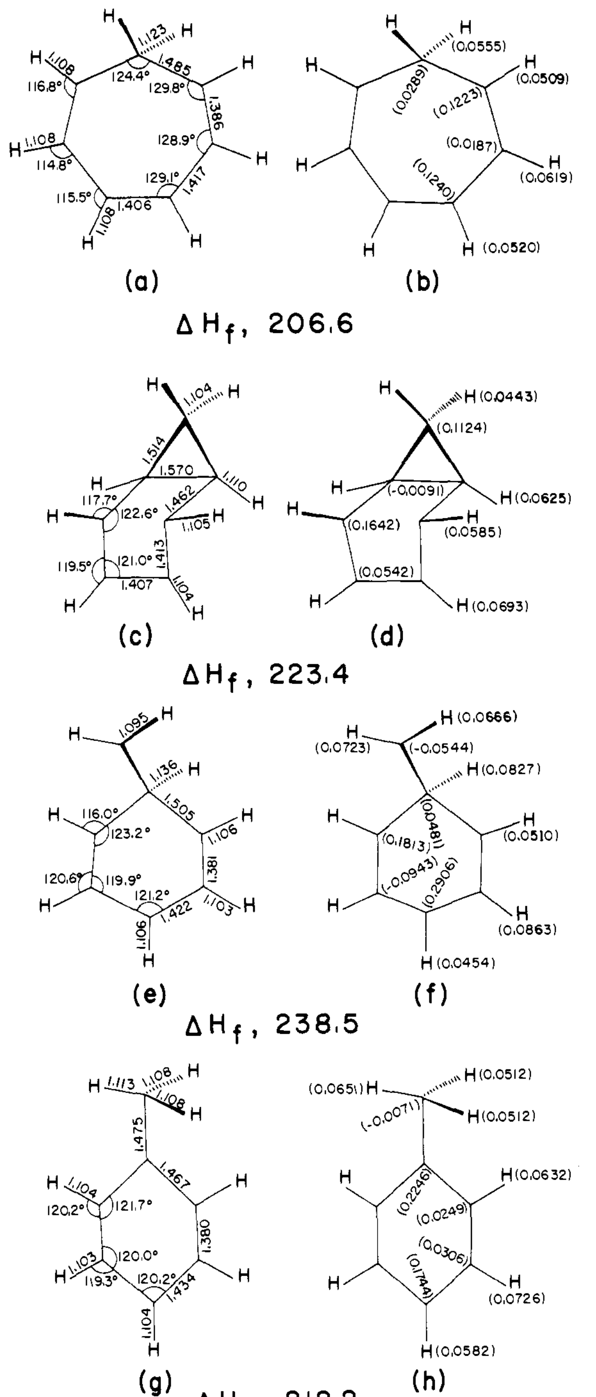


Figure 1. Calculated geometries, heats of formation (ΔH_f, kcal/mol at 25 °C), and distributions of formal charge: (a) (b) for **6**; (c) (d) for **10**; (e) (f) for **11**; (g) (h) for **5**.

The hexatriene system in **2** is severely twisted out of planarity,[17] the dihedral angles between adjacent double bonds being no less than 54°. Since the HOMO of hexatriene is a π MO with nodes intersecting the "single" bonds, removal of an electron from it should greatly increase the π orders of the "single" bonds while decreasing those of the "double" ones. The hexatriene molecular ion should therefore have a much greater tendency to planarity than hexatriene itself. Since the difference in energy between **2** and planar **2** (i.e., the barrier to inversion in **2**) is known to be small, the corresponding molecular ion (**6**) should then be planar, and MINDO/3 indeed predicts this to be the case. Vertical ionization of **2** should therefore lead to **6** in a very unfavorable nonplanar geometry. There should therefore be an unusually large difference between the vertical and adiabatic ionization potentials of **2**, as MINDO/3 indeed predicts. Now Bischof and Heilbronner[18] have measured the vertical ionization potential of **2** accurately and unambiguously by photoelectron spectroscopy, finding it to be 8.57 eV. This is only 0.05 eV greater than the electron impact value, which must therefore be much greater than the adiabatic ionization potential. The heat of formation of **6** must therefore be much less than the "experimental" value in ref 10. This discrepancy would not be surprising if **6** indeed has a planar geometry because extrapolation of the mass spectral ion current to the limit corresponding to the onset of ionization would be virtually impossible.

Batich, Bischof, and Heilbronner[18] have developed an apparently very successful semiempirical treatment of the relation between the vertical ionization potentials of polyenes and their distortion from coplanarity. Using their values, one can estimate the vertical ionization potential of planar **2** to be 7.8 eV so the corresponding adiabatic value is probably close to 7.5 eV. Since the difference in energy between **2** and planar

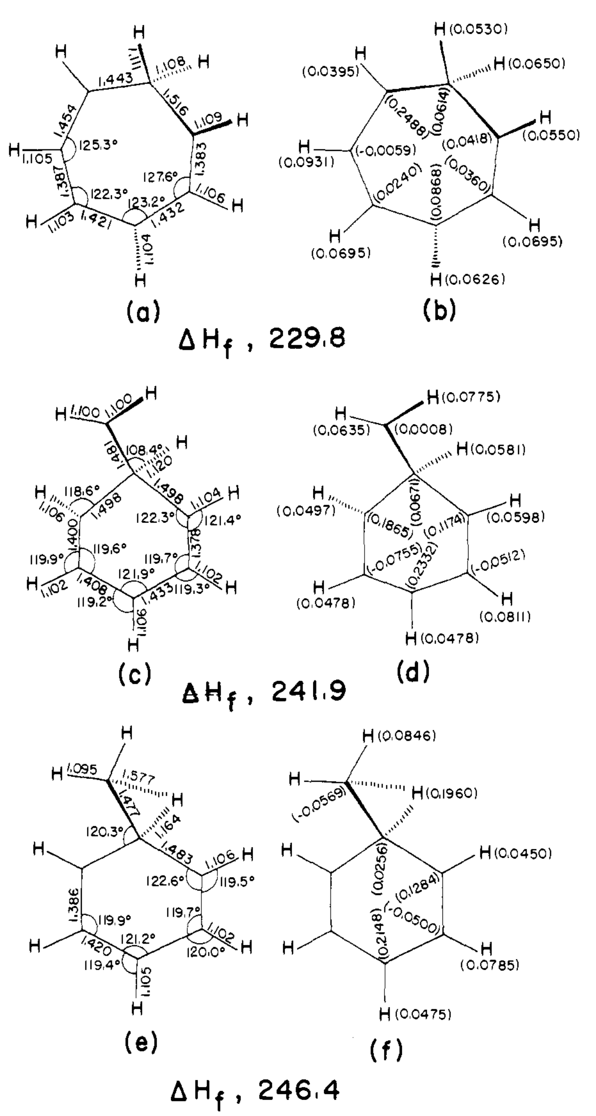


Figure 2. Calculated geometries, heats of formation (ΔH_f, kcal/mol at 25 °C), and distributions of formal charge in the transition states (a) (b) for [**6** → **10**]; (c) (d) for [**10** → **11**]; (e) (f) for [**11** → **5**].

2 is known to be small, being equal to the barrier to inversion, the adiabatic ionization potential of **2** itself cannot then be much greater than 7.5 eV, supporting the MINDO/3 estimate and hence the MINDO/3 value for the heat of formation of **6**.

MINDO/3 has been shown[9] to give heats of formation for cations and radicals that are in as good agreement with experiment as those for normal molecules and we have recently found that it also gives good results for radical cations. It is therefore difficult to believe that the MINDO/3 estimate of the difference between the vertical and adiabatic ionization potentials of **2** could be greatly in error, depending as it does on calculations for the same ion (**6**) in two different geometries.

As an additional check, we calculated the energy of the ion formed by vertical ionization directly, i.e., **6** with the geometry corresponding to **2**. Since MINDO/3 gives estimates of the dihedral angles in **2** that are too small, and since the energy of **6** depends critically on these, we used the geometry determined experimentally[16] for **2** in our calculation. The calculated heat of formation (235 kcal/mol) agreed quite closely with that (24 kcal/mol) estimated from the observed heat of formation of **2** (43.9 kcal/mol) and its measured vertical ionization potential (8.57 eV).

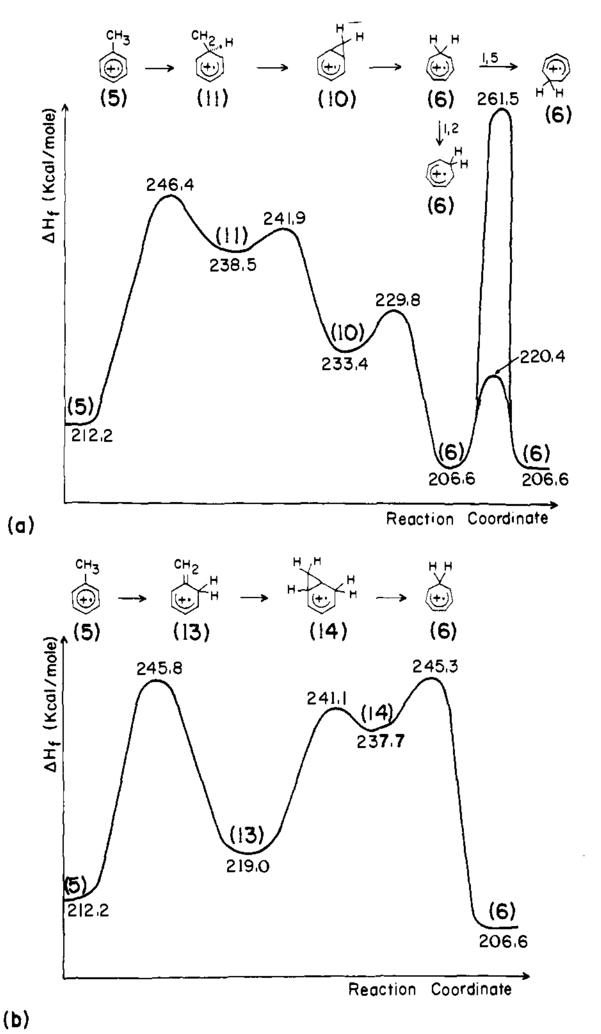


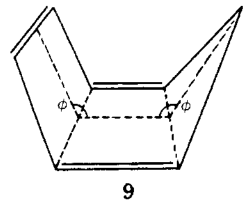
Figure 3. Calculated MERP (a) for **5** → **11** → **10** → **6** → (1,2- or 1,5-hydrogen shift in **6**), (b) for (**5** → **13** → **14** → **6**).

In all, it seems likely that the true heat of formation of **6** is greater than our calculated value but very much less than the published "experimental" one. We believe it to lie somewhere in the range 215-220 kcal/mol.

(2) **Skeletal Rearrangements.** Hoffman[3] has suggested that carbon scrambling can occur in the $C_7H_8^{+\cdot}$ ions by the series of reactions (**6** $\rightleftarrows$ **10** $\rightleftarrows$ **11** $\rightleftarrows$ **5**). Figure 1 shows the geometries and distributions of formal charge calculated for **10** and **11** while Figure 2 gives similar information for the transition states [**6** → **10**], [**10** → **11**], and [**11** → **5**]. Figure 3a indicates the energy profile for this series of reactions, the heats of formation of the various species being listed in Figures 1 and 2.

The norcaradiene radical cation (**10**) has the expected bent geometry, while **11** corresponds, again as expected, to the radical cation formed by loss of a hydrogen atom from the methyl group of methylbenzenium (**12**). The predicted formal positive charges in **11** follow the pattern predicted on this basis, being large in the ortho and para positions with the latter predominating.

The structures calculated for the various transition states also seem reasonable and the heats of formation calculated for them and for the stable intermediates are consistent with Hoffman's mechanism[3] (see Figure 3a). The calculated overall activation energy for (**6** → **5**) is 39.8 kcal/mol and the calculated overall heat of reaction is +5.6 kcal/mol. Given enough excess energy, **5** and **6** should equilibrate easily. As might have been expected, **11** is the least stable of the four species (**5**, **6**, **10**, **11**) and the highest transition state for the overall reaction corresponds to the step (**11** → **5**).



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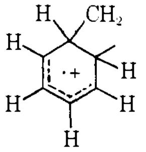

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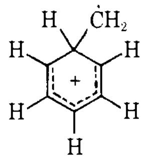

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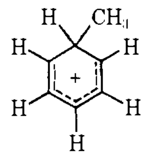

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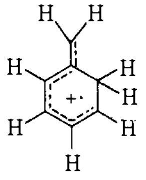

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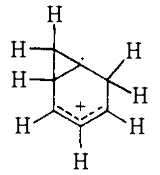
As McLafferty et al.[7] have pointed out, 5 could also rearrange by an alternative hydrogen shift, this time from methyl to an ortho position to give **13**. Intramolecular cyclization of **13** to **14**, followed by a 1,2-hydrogen shift to **10** and ring opening to **6**, would then provide an alternative route from **5** to **6**. We also studied this series of reactions.

Figures 4a–d show the geometries, heats of formation, and distribution of formal charge for **13** and **14**. The MINDO/3 heat of formation for **13** (219.0 kcal/mol) is in agreement with an experimental estimate (<225 kcal/mol[19]). According to MINDO/3, the conversion of **14** to **6**, by migration of a hydrogen from the methylene group in the six-membered ring to the adjacent bridgehead carbon, followed by ring expansion, takes place in a single kinetic step. Although **10** is predicted to be a stable species, it does not appear as an intermediate in the conversion of **14** to **6**. Figures 5a–f show the geometries, heats of formation, and distributions of formal charge calculated for the transition states [**5** → **13**], [**13** → **14**], and [**14** → **6**], while Figure 3b shows the reaction profile for the overall conversion (**5** → **13** → **14** → **6**). Note that the distribution of formal charge in **14** corresponds to the indicated classical structure, a combination of an allyl cation with a tertiary alkyl radical.



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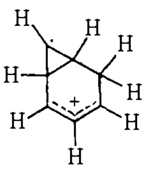

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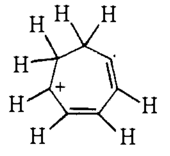

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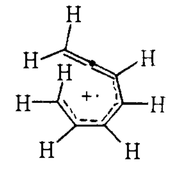

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The overall activation energy for the rearrangement of **5** to **6** via **13** and **14** (33.6 kcal/mol) is a little less than that for rearrangement via **11** and **10** (34.2 kcal/mol; see Figure 3a), but the difference is too small to be significant. Both processes are likely to take place with comparable ease. Either or both, if rapid and reversible under the conditions in the mass spectrometer, could lead to the observed carbon scrambling (cf. ref 7 and 20).

We also examined two other possible reactions of the radical ion **13**.

The first involved an alternative 1,2 migration of hydrogen, from the methylene group in the three-membered ring, to form **15** followed by ring opening to **6**. Figure 5g and 5h show the geometry, heat of formation, and distribution of formal charge

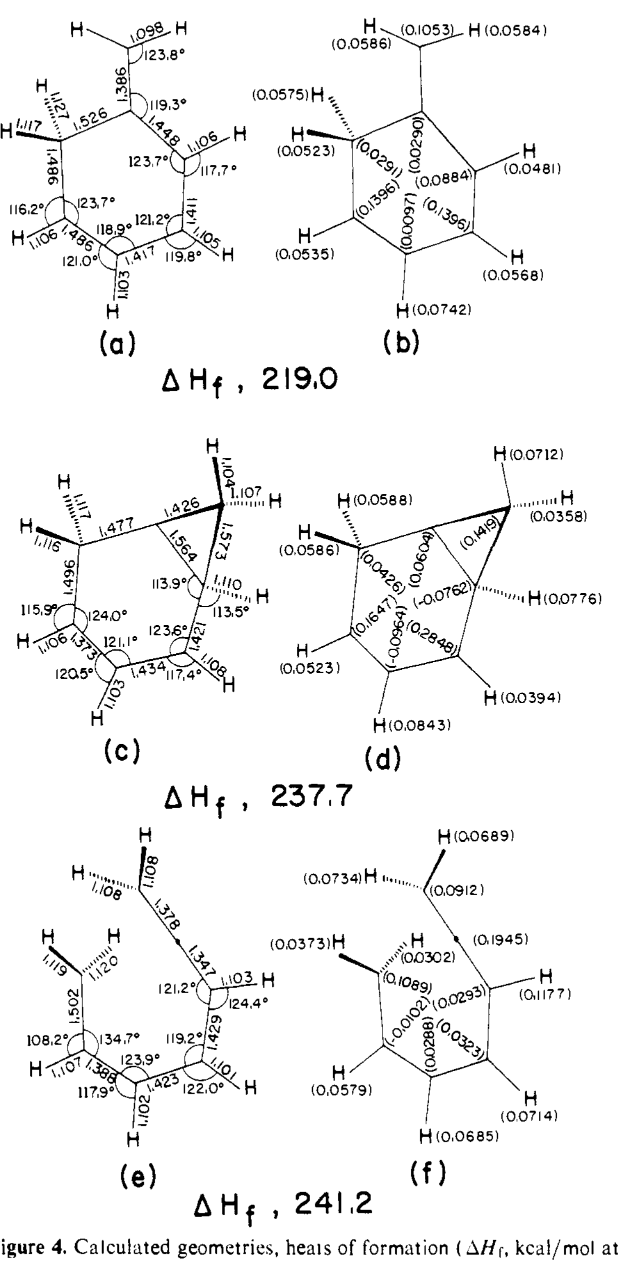


Figure 4. Calculated geometries, heats of formation (ΔH_f, kcal/mol at 25 °C), and distributions of formal charge (a) (b) for **13**, (c) (d) for **14**, (e) (f) for **17**.

for the transition state in this reaction, which again leads directly to **6**. This path is, as one might have expected, much less favorable than reaction by the alternative 1,2-hydrogen shift (cf. (**14** → **6**) above), the activation energy being over 20 kcal/mol greater than for the latter. It therefore seems unlikely that it can play any important role.

A second possible route from **13** to **6** seemed to be a Wagner-Meerwein-like rearrangement of **13** to **16**, which would undoubtedly rearrange to **6** by a 1,2-hydrogen shift. According to MINDO/3, however, **16** is not a stable species, the only product being the open chain ion **17** whose properties are shown in Figures 4e and 4f. While the heat of formation calculated for **17** is reasonably low, that for the transition state [**13** → **17**] is very high, certainly >261 kcal/mol. In view of this, and in view of the fact that the conversion of **13** to **17** seemed unlikely to form part of any scrambling process, we did not locate this transition state precisely. This path, i.e., (**5** → **13** → **17**), does, however, provide an attractive mechanism for fragmentation of $C_7H_8^{+\cdot}$ ions, which occurs readily in the mass spectrometer.

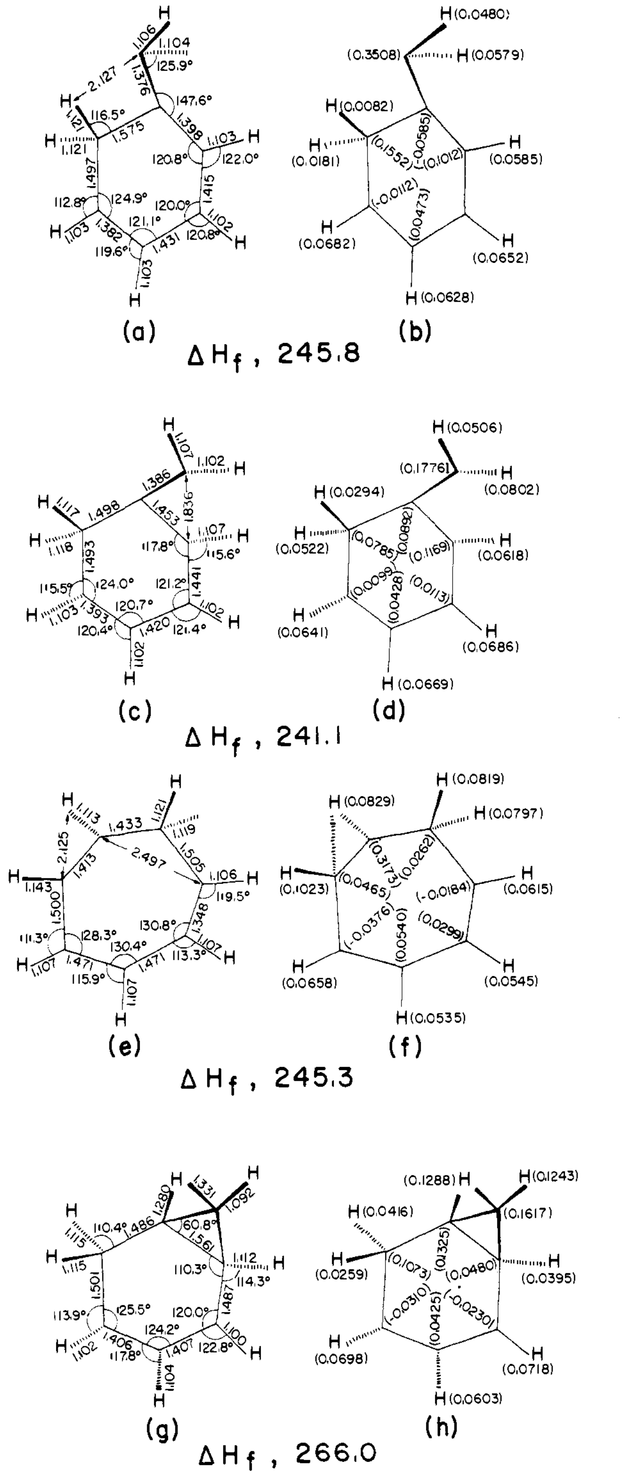


Figure 5. Calculated geometries, heats of formation (ΔH_f, kcal/mol at 25 °C), and distributions of formal charge in the transition states (a) (b) for [**5** → **13**], (c) (d) for [**13** → **14**], (e) (f) for [**14** → **6**], (g) (h) for [**14** → **15**].

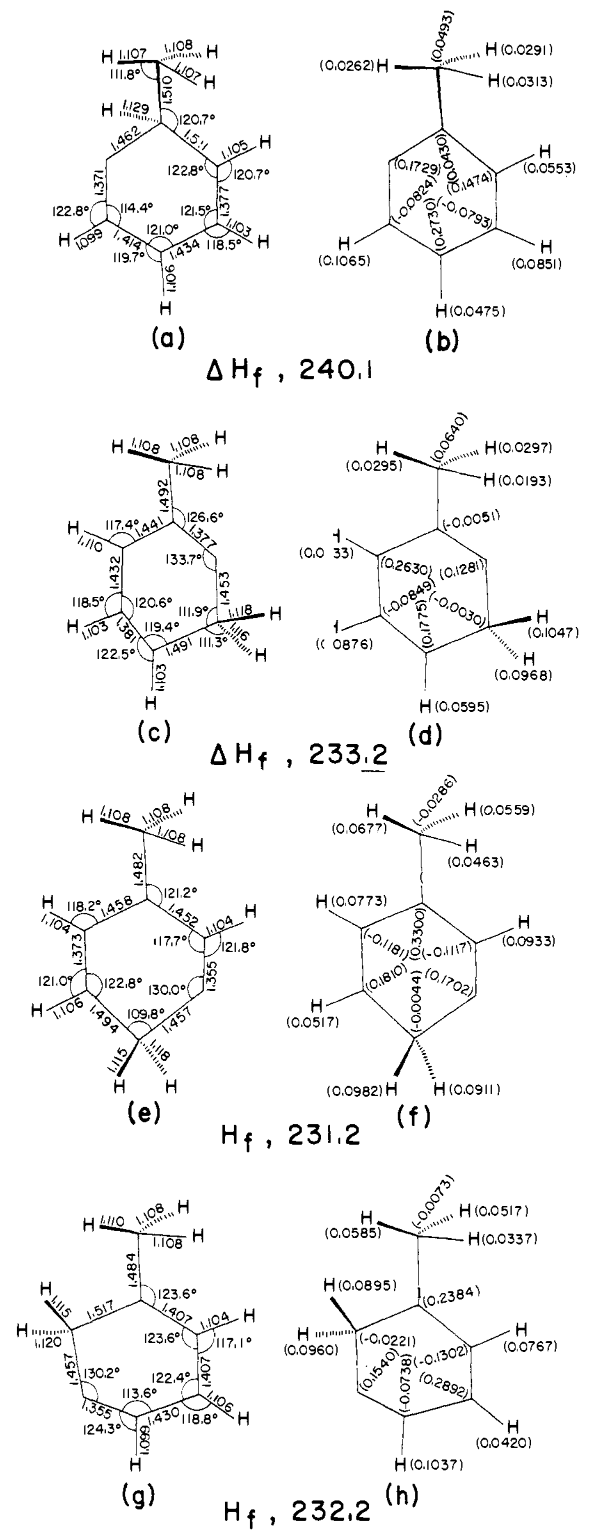


Figure 6. Calculated geometries, heats of formation (ΔH_f, kcal/mol at 25 °C), and distributions of formal charge (a) (b) for **18**, (c) (d) for **19**, (e) (f) for **20**, (g) (h) for **21**.

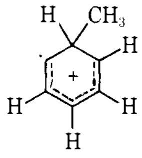
(3) **Hydrogen Scrambling.** It is well known[2,3] that complete hydrogen scrambling is observed in most of the ions derived by fragmentation of $C_7H_8^{+\cdot}$. Recently, however, McLafferty et al.[7] have found an exception in the ions formed by loss of one carbon atom from the TMI (**5**), the scrambling of hydrogen atoms from the methyl group with the ring being incomplete. Their results[7] seemed to indicate that scrambling of the methyl hydrogens takes place by two different mechanisms, one leading to indiscriminate scrambling with the ring while the other leads to scrambling only with the ortho hydrogen atoms. They suggested[7] that the latter process involved the reversible interconversion (**5** → **13**) while the former involves interconversion of **6** and **5** by one of the paths indicated in Figure 3. Our results strongly support this suggestion.

In the rearrangement of **5** to **6** via **11** and **10**, the overall transition state corresponds to the first step (**5** → **11**) and the energies of the transition states for the subsequent steps are much less (see Figure 3a). The interconversion (**10** ⇄ **11**) should therefore be easier than reversion to **5** and should lead to complete equilibration of all the hydrogen atoms in the ring. The result will be indiscriminate scrambling of the methyl and ring hydrogens.

In the alternative route from **5** to **6** via **13** and **14**, the transition states of all three steps are very similar (Figure 3b). Indeed, since **14** contains a strained three-membered ring, the heat of formation calculated for it by MINDO/3 is probably somewhat too low, and if so, the calculated barrier for rearrangement (**14** → **6**) is probably also too low. Therefore **13** will probably revert to **5** more easily than it rearranges to **6**. A similar argument applies in the case of **10** in the alternative reaction path from **5** to **6**; however, as Figure 3a indicates, this would not alter our argument because the conversion of **10** to **6** would still involve a much lower barrier than reversion to **5**. Reversion of **13** to **5** should therefore compete effectively with rearrangement to **14**, and the interconversion (**5** → **13**) scrambling the methyl hydrogens only with those in the ortho positions.

These reactions could account for the complete scrambling of hydrogen atoms in $C_7H_8^{+\cdot}$ that has been established by labeling and double labeling experiments.[2,3,7] We have, however, also examined a number of other possible processes.

First we considered the possible interconversion of the species **18–21**, derived from **5** by 1,2 migrations of hydrogen atoms in the ring. Figure 6 shows the geometries, heats of formation, and distributions of formal charge calculated for the various ions. The energies of **19**, **20**, and **21** are virtually identical while that of **18** is greater by ca. 8 kcal/mol. The distribution of formal charge in each ion follows the same pattern as that in **11**.



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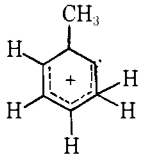

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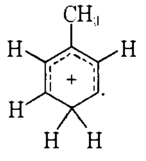

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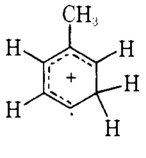

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Figure 7 shows the corresponding properties calculated for the transition states [**5** → **18**], [**5** → **19**], [**5** → **20**], and [**5** → **21**]. Each corresponds to a protonated tolyl radical, with HC bond lengths ranging from 1.200 to 1.494 Å for the bridging hydrogen atoms. The geometry and charge distribution in each corresponds to that expected for a π complex.

The highest heat of formation for any of these transition states is 242.6 kcal/mol, i.e., several kilocalories per mol less than that of either of the two carbon scrambling processes (Figure 3). McLafferty et al.[7] have presented evidence indicating that scrambling of the hydrogen atoms in the ring of **5** is faster than skeletal rearrangement. Our calculations are clearly consistent with this result and suggest that the ring scrambling occurs by 1,2-hydrogen shifts, rather than by 1,2-hydrogen shifts together with valence isomerization as in the mechanism suggested by McLafferty et al.[7] While we have not carried out calculations for the $C_6H_6^{+\cdot}$ system, it seems very likely that the observed scrambling of hydrogen is due to analogous hydrogen shifts rather than to skeletal rearrangements via molecular ions of benzene valence isomers. The activation energies for the latter would certainly be much greater than those calculated here for rearrangement of **5** via **18–21** (≤30.4 kcal/mol).

The hydrogen migrations involved in rearrangement by our mechanism could be described as a *hydrogen ring walk*.

The next hydrogen scrambling mechanism considered was that suggested by Hoffman,[3] involving 1,5-hydrogen shifts in **6**. Figures 8a and 8b show the geometry, heat of formation, and distribution of formal charge calculated for the corresponding transition state, **22**. This has the expected (C_v) symmetry, with corresponding distortion of the seven-membered ring out of the plane, and the lengths (1.330 Å) of the CH bonds of the migrating hydrogen seem reasonable. The calculated heat of formation is, however, very high, corresponding to an activation energy of 55 kcal/mol. It therefore seems unlikely that hydrogen scrambling can occur to any great extent by this route. This is in remarkable contrast to the corresponding 1,5-hydrogen rearrangements in cycloheptatriene (**2**) itself which

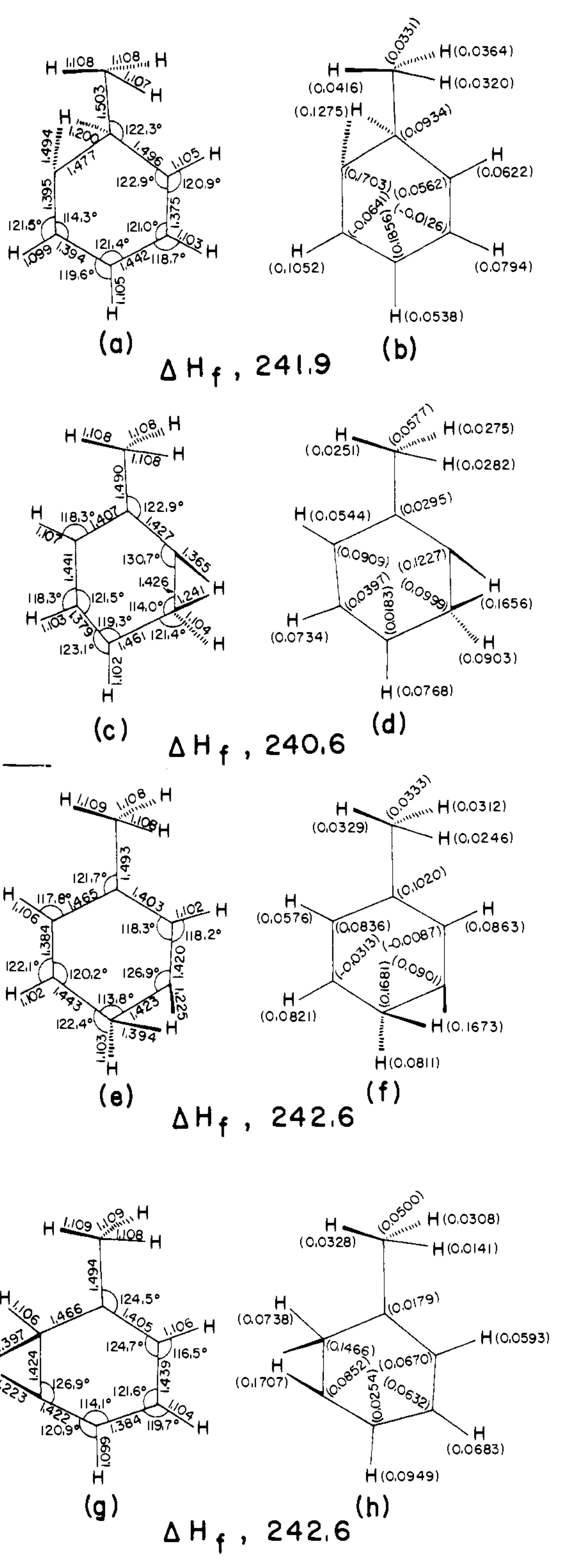


Figure 7. Calculated geometries, heats of formation (ΔH_f, kcal/mol at 25 °C), and distributions of formal charge in the transition states (a) (b) for [**5** → **18**], (c) (d) for [**5** → **19**], (e) (f) for [**5** → **20**], (g) (h) for [**5** → **21**].

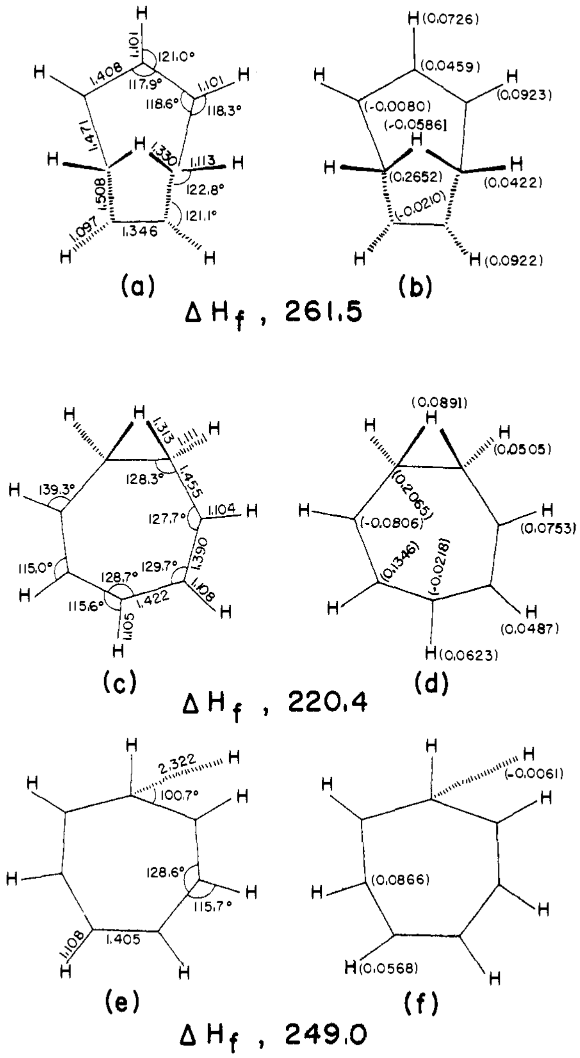
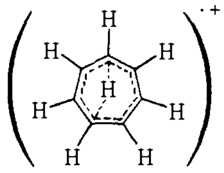


Figure 8. Calculated geometries, heats of formation (ΔH_f, kcal/mol at 25 °C), and distributions of formal charge in the transition states (a) (b) for 1,5-hydrogen shift in **6**, (c) (d) for 1,2-hydrogen shift in **6**, (e) (f) for hydrogen dissociation in **6**.

occur very easily indeed.[21] The difference arises from the same factor involved to explain the difference between the calculated and observed heats of formation of **6**. In order to get to the transition state for 1,5-hydrogen migration in **2**, the ring must be buckled much more than it is even in **2** itself. This distortion will very greatly increase the ionization potential and so correspondingly increase the energy of the transition state for 1,5-hydrogen migration.



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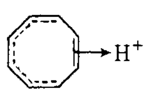


23

Next we examined the alternative possibility of a 1,2-hydrogen shift in **6**. Figures 8c and 8d show the properties calculated for the corresponding transition state. The calculated geometry and charge distribution show this to correspond to the π complex structure indicated in **23**, i.e., an olefin–proton π complex combined with a pentadienyl radical. The calculated heat of formation is very much less than that for **22**, corresponding to an activation energy of only 14 kcal/mol. This is very much less than the activation energies calculated for the other possible rearrangements of **6** (see Figure 3) and we therefore expect hydrogen equilibration to be rapid in **6** under conditions of excitation mild enough to avoid skeletal rearrangements. Here again the difference from **2** is noteworthy, 1,2-hydrogen migration in the latter being very much more difficult[21] than 1,5. The difference can be explained in a similar way, in terms of the relative ionization potentials of **2**, **6**, and the corresponding transition states.

McLafferty et al.[7] have indeed found that scrambling of hydrogen in **6** is fast compared with loss of a one-carbon unit, presumably implying that the hydrogen scrambling is faster than skeletal rearrangement. This of course is in complete accord with our results.

(4) Hydrogen Atom Dissociation from $C_7H_8{}^{+\cdot}$ Ions. In order to complete this MO investigation of the $C_7H_8{}^{+\cdot}$ ion surface, the activation energies for loss of a hydrogen atom from CHMI (**6**) and TMI (**5**) were calculated. Figures 8e and 8f show the geometry, heat of formation, and formal charge distribution for the transition state corresponding to loss of a hydrogen atom from **6**. The departing hydrogen atom is quite distant from the $C_7H_7{}^+$ ("tropylium") ring (2.322 Å), although the transition state does not indicate a symmetrical cleavage. The heat of formation calculated for the transition state (249.0 kcal/mol) is very nearly equal to the heat of formation of the products as calculated[22] by MINDO/3 (247.6 kcal/mol). Thus the reverse activation energy is small (1.4 kcal/mol).

While the hydrogen atom dissociation from TMI (**5**) was investigated, the transition state was not located precisely. From our calculations it was obvious that the reverse activation energy was small, giving an upper limit[22] of about 272 kcal/mol for the heat of formation of the transition state.

Our calculations therefore suggest that in the mass spectrometer, TMI (**5**) will undergo rearrangement to other $C_7H_8{}^{+\cdot}$ species by one of the mechanisms indicated above more easily than it will lose hydrogen to form benzyl cation (**4**). Furthermore, the easiest route from **5** to tropylium ion (**3**) is predicted to be via the CHMI (**6**). These conclusions would not be altered if tropylium has the heat of formation reported by Thrush et al.[23] (209 kcal/mol; see ref 10), although, as noted in part 1, this value is probably too high.

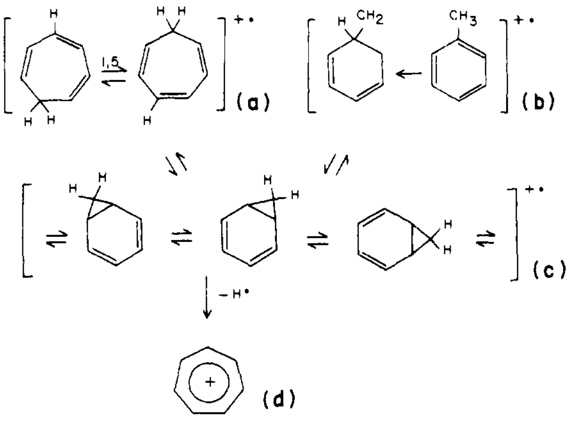
Summary

Our calculations lead to the following conclusions:

(a) Starting from TMI (**5**), it is more likely there will be ring hydrogen exchange rather than benzylic to ring hydrogen exchange (i.e., there is preferential scrambling of protons).

(b) The ion **5** can rearrange to **6** via either paths through α-hydrogen (Hoffman mechanism[3]) or *o*-hydrogen shifts (cyclohexadienyl ion (**13**) mechanism).

Scheme I



(c) Scrambling of hydrogen atoms in CHMI (**6**) is very rapid via 1,2-hydrogen shifts, so that starting from an appropriately labeled cycloheptatriene it may be possible to observe hydrogen scrambling without carbon scrambling.

(d) Loss of a hydrogen atom to give a $C_7H_7^+$ (*m/e* 91) moiety is more likely through **6** rather than **5**.

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Theoretical Studies of the Photochemistry of Acyclic Azoalkanes

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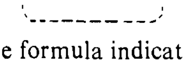
Abstract. Nonempirical molecular orbital calculations have been carried out on the S_0 (ground), S_1, T_1, and T_2 states of azomethane and on selected states of diimide and azoethane. Potential energy surfaces for several possible isomerization pathways from trans to cis isomers have been obtained. Motions in which one alkyl group rotates about the N═N bond or moves in the N═N—R plane through a linear configuration appear to be of considerable importance, while the motion which simultaneously linearizes both N═N—R groups is forbidden by a substantial energy barrier. Spectral and thermodynamic quantities calculated are in good agreement with the experimental data where available. The shapes of the energy surfaces provide explanations for such phenomena as the lack of observed fluorescence and phosphorescence in acyclic azoalkanes and the variation in the quantum yields of isomerization and dissociation with pressure and with the method of excitation.

I. Introduction and Background

In recent years there have been extensive experimental studies of the thermal and photochemical behavior of azoalkanes,[2-5] which have the general formula



$$R—N{=}N—R'$$

The dashed line in the formula indicates that the compound may be cyclic. While there have been several detailed theoretical investigations[6-9] of the prototype molecule diimide (R = R′ = H), calculations on the larger and more stable azo compounds have been almost nonexistent.[10] The chemistry of diimide is significantly different from that of azoalkanes,[11] so calculations on a molecule like azomethane (R = R′ = CH_3) should provide a sounder model for understanding the properties of azo compounds of moderate complexity. In this paper we report on a series of such calculations which have been undertaken in an attempt to elucidate several aspects of the thermal and photochemical behavior of acyclic azoalkanes. We focus here primarily upon the static properties (geometry, spectra, etc.) and upon the mechanism of cis-trans isomerization. The interesting and important problem of decomposition into molecular nitrogen and radical products is mentioned only briefly, but will be discussed more fully in a later paper.

The computational technique employed in this work is the partial retention of diatomic differential overlap (PRDDO) method of Halgren and Lipscomb.[12] This self-consistent nonempirical technique affords accuracy comparable to that of more elaborate minimal basis set self-consistent-field (SCF) approaches, but with computation times only slightly longer than those of much less accurate semiempirical methods. Details of the calculation are discussed briefly in the next section, and the results are presented and analyzed in section III.

Before proceeding with the main results of this work, it will be useful to summarize some of the more important features of the properties and the photochemistry of acyclic azoalkanes which we shall seek to explain in subsequent sections.

(i) At low pressures in the gas phase, $n_- \rightarrow \pi^*$ excitation of acyclic azoalkanes results in photodissociation to N_2 and alkyl radicals with quantum yields approaching unity.[13]