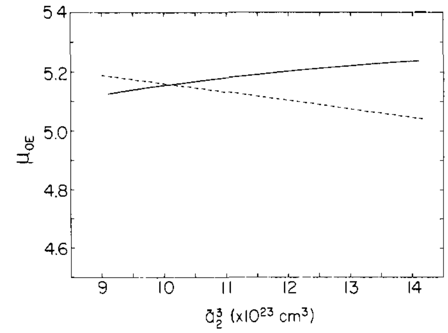

Figure 4. The dipole moment of *all-trans*-retinal calculated by using eq 1 as a function of $\bar{a}_2^3$. The dashed curve is obtained by varying only $\bar{a}_2^3$ and holding all other parameters constant. The solid curve is obtained by varying $\bar{a}_2^3$ and including the effects that variations in $\bar{a}_2^3$ have on $\partial\epsilon/\partial\phi_2$ and ϵ_2^{∞}. (ϵ_2^{∞} is determined from solution refractive index measurements and it varies with the cavity radius through the $\partial\epsilon^2/\partial\phi_2$ term in eq 4.) Remaining parameters in eq 1 are set equal to those determined for *all-trans*-retinal in hexane (see Table I).

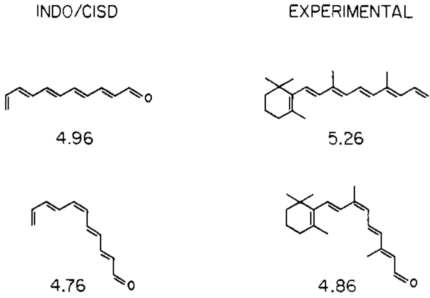

Figure 5. A comparison of theoretical (left) and experimental (right) dipole moments. The experimental values for *all-trans*-retinal (above) and 9-*cis*-retinal (below) are the μ_{OE} values given in Table II, with ϵ_2^{∞} for 9-*cis*-retinal assumed to be equal to ϵ_2^{∞} for *all-trans*-retinal. The theoretical values are taken from ref 30.

11-cis must be too small because the 11-cis isomer, in either conformation, is more spherical than *all-trans*-retinal. Furthermore, the relative contribution of the dipole moment to the dielectric constant will be greater for the 12-s-cis conformer than for the more polar but less spherical 12-s-trans conformer, making it even more difficult to obtain information about the relative populations of the conformers from dielectric measurements alone.

Dipole moments determined from solution dielectric data cannot be depended upon to be very exact, even when ellipsoidal cavity formalisms are used. The retinal isomers are particularly difficult to analyze because their large electronic polarizabilities are not accurately known and their molecular geometries are such that the cavity shapes cannot be determined unambiguously. Figures 1 through 4 illustrate the changes in the calculated dipole moment which result from altering the various parameters in eq 1. All of the parameters except the one to be varied are set equal to those determined for *all-trans*-retinal in hexane. Each figure demonstrates the effect on μ_{OE} of changes in one parameter (A_a, ϵ_2^{∞}, $\partial\epsilon/\partial\phi_2$, or $\bar{a}_2^3$) over a range of values which might reasonably be estimated or experimentally determined for use in dipole moment calculations on retinal isomers. The remaining parameters in eq 1, ϵ_1 and T, are normally known with sufficient accuracy that uncertainties in these parameters are insignificant sources of error. These figures underscore the importance of making accurate determinations of ϵ_2^{∞} and A_a. Unfortunately, estimates of A_a for the same molecule can vary greatly depending upon whether or not the solute is allowed to rotate to define the cavity and whether average or maximum molecular dimensions are used. Dielectric constants can be determined with sufficient accuracy that errors in ϵ_2^{∞} and A_a probably account for most of the error in dipole moment determinations on elongated polyenes like retinal.

Molecular orbital calculations on the polyene chain alone predict dipole moments of 4.96 D for the all-trans isomer and 4.76 D for the 9-cis isomer. These calculations were carried out by using the INDO-CISD formalism, an all-valence electron semiempirical molecular orbital theory including restricted single (~200) and double (~400) excitation configuration interaction.[30] The difference between the calculated and observed values are due in part to neglect of the methyl groups and the β-ionylidene ring; inclusion of the latter would increase the calculated dipole moments. The calculated dipole moments are, therefore, consistent with the observed values. The theoretical and experimental results are summarized in Figure 5.

Acknowledgment. This work was supported in part by grants to R.R.B. from the National Institutes of Health (EY-02202), the National Science Foundation (CME-7916336), and the Committee on Research, University of California, Riverside. A.B.M. gratefully acknowledges a University of California President's Undergraduate Research Fellowship.

A MINDO/3 Theoretical Study on Structure, Fragmentation, and Scrambling Reaction in $C_6H_5^+$[1]

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Abstract: The structures, fragmentations, and scrambling reactions in the $C_6H_5^+$ system were examined by using the MINDO/3 method. The stable structures are the phenyl cation and its linear isomers. The activation energies of fragmentation from those ions were calculated. In the phenyl cation the cleavage that involves the β bond to the carbon atom with the formal cation requires lower energy than that of the α bond, indicating applicability of fragmentation rules in organic mass spectrometry to aromatic ring systems. The lowest activation energy for the loss of C_2H_2 from the phenyl cation is determined to be 108 kcal/mol. The calculated energies of interstructural conversions suggest a flexible nature of mutual conversion. One of the lowest energies for complete scrambling of carbon atoms in the phenyl cation was estimated to be less than 69 kcal/mol. This value is far lower than that of fragmentation, explaining complete scrambling of carbon atoms prior to the fragmentation of $C_6H_5^+$ ion which is produced from iodobenzene.

The fragmentation rules in organic mass spectrometry have developed from the relationship between geometrical structure, stability, and electronic structure of the system in both the initial and final states.[2] However, when it comes to the problem of aromatic rings, this is not the case even in the simple phenyl cation because the ion structure is quite uncertain. The phenyl cation ($C_6H_5^+$) is assumed to have been frequently observed in organic mass spectrometry. This ion usually gives the $C_4H_3^+$ ion, losing acetylene. Harrison[3] and Rosenstock et al.,[4] summarizing the heats of formation of $C_6H_5^+$ ions from a variety of molecules and the phenyl radical, suggested the existence of various structures of the ion.

Several MO studies have dealt with the electronic structure of the phenyl cation.[5-8] The geometrical structures have been determined theoretically with the INDO[7] and ab initio STO-3G[8] methods, but the accuracy is very limited even in the latter method.[9] Moreover, the number of geometrical isomers of $C_6H_5^+$ cited there is too small to figure out the overall nature of the ions. According to the comment cited by Dill et al.,[8] Haselbach and Bally have calculated more than 40 isomers of the $C_6H_5^+$ system by using MINDO/3. Although we have awaited the report since 1976, such a report has not appeared yet. Meanwhile Castenmiller and Buch[10] have reported the potential energies of the nonlinear $C_6H_5^+$ systems by using MINDO/3, where unfortunately the geometry optimization concerning the hydrogen atom was omitted. Besides, the discussion is not oriented to fragmentation. Since, as will be mentioned later, the hydrogen-bridged structures in cation are often more stable than the corresponding classical structures, such a neglect is not very acceptable in this kind of study. Therefore, we describe here our results of structure calculations and discuss the potential energies of fragmentation, interstructural conversion, and scrambling reaction, hoping that it might give some suggestions to the blind point of fragmentation rules for organic compounds.

Method

There must be criticism against adopting semiempirical MO methods for the calculation of ions, since apparently the parameters in semiempirical MO theories have been determined such that the theories might give appropriate results for neutral molecules. Nevertheless, we adopted MINDO/3 for the following reasons. First, H- or C-bridged structures are often stable in ions. In such cases electron correlations play important roles in total energy. Since the Hartree–Fock method with a single determinant cannot take the correlations into account, it results in underestimating the relative stability of the bridged structure. This comes to be important when small differences of total energies or heats of formation are of interest. However, well-parametrized semiempirical SCF MO methods such as MINDO/3 successfully incorporate the effect of the correlations in empirical parameters;[11] the MINDO/3 method correctly predicts the stabilities of $C_2H_3^+$ and $C_3H_7^+$ ions whereas even the considerably sophisticated 6-31G* fails.[9b,c] Secondly, a number of ions have so far been calculated by MINDO/3 to give acceptably accurate heats of formation. Finally, since geometry optimization is inevitable in ions, the calculation by the sophisticated ab initio theories is, at present, not feasible for a system as large as $C_6H_5^+$. The isomers of the phenyl cation cited here have been calculated by the MINDO/3 program[12] with the Davidon–Fletcher–Powell procedure,[13,14] where all geometrical parameters were taken into account in the optimization.

Table I. Heats of Formation in the $C_6H_5^+$ System by the MINDO/3 Method (kcal/mol)

structure no.	ΔH_f[a]	ΔE[b]	ΔH_f[c]
1	244.8	0.0	244.8
2	259.4	14.6	
3	260.4	15.6	
4	273.0	28.2	281.4
5	281.5	36.7	281.6
6	284.8	40.0	
7	285.2	40.4	
8	292.6	47.8	294.8
9	298.5	53.7	298.7
10	299.2	54.4	299.5
11	306.8	62.0	307.6
12	313.1	68.3	
13	331.2	86.4	355.6
14	427.9	183.1	

[a] This work. [b] Relative energy. [c] Reference 10.

Results and Discussion

Structures and Relative Energies. The structure of the benzene ion has been the subject of many studies ever since the similarity between the mass spectra of benzene and 1,3-hexadien-5-yne has been pointed out.[15] A similar question can naturally be posed for the phenyl cation. Figure 1 and Table I show 14 isomers of the $C_6H_5^+$ system and their heats of formation and relative energies, respectively. New measurements bearing on $C_6H_5^+$ have made it clear that the phenyl cation has a heat of formation in the range 266–270 kcal/mol, and the structure would be a cyclic one since the lowest value has been obtained from the phenyl radical.[16] Although our calculation supports this, the calculated value for **1** is too low compared to that of the experiment (266 kcal/mol[16]). As Cone et al.[17] suggested in the tropylium ion, this difference (21 kcal/mol) would be explained by the geometrical difference between the radical and ionic states rather than by any error in the MINDO/3 method.

Experimental measurements of heat of formation is most conveniently done by measuring the ionization potential of the radical A· using eq 1, where $\Delta H_f(\mathrm{A}\cdot)$ and $I_p(\mathrm{A}\cdot)$ are the heat of

$$\Delta H_f(\mathrm{A}^+) = I_p(\mathrm{A}\cdot) + \Delta H_f(\mathrm{A}\cdot) \qquad (1)$$

formation and the ionization potential of A·, respectively. Since ionization by electron impact or photon impact is a vertical process, the heat of formation by this method (we call it vertical heat of formation in this paper) does not refer to that of the vibrational ground-state ion but does correspond to the ion with the same geometry as the radical. In order to ensure this, calculation on the phenyl radical has been carried out to give the geometry which is not so different from benzene (Figure 2).[18] If this is compared with **1** in Figure 1, a considerable difference of structure between them is determined. Therefore, naturally, the calculated heat of formation does not agree with the vertical heat of formation. Since this might be generally true, one must be careful when the ex-

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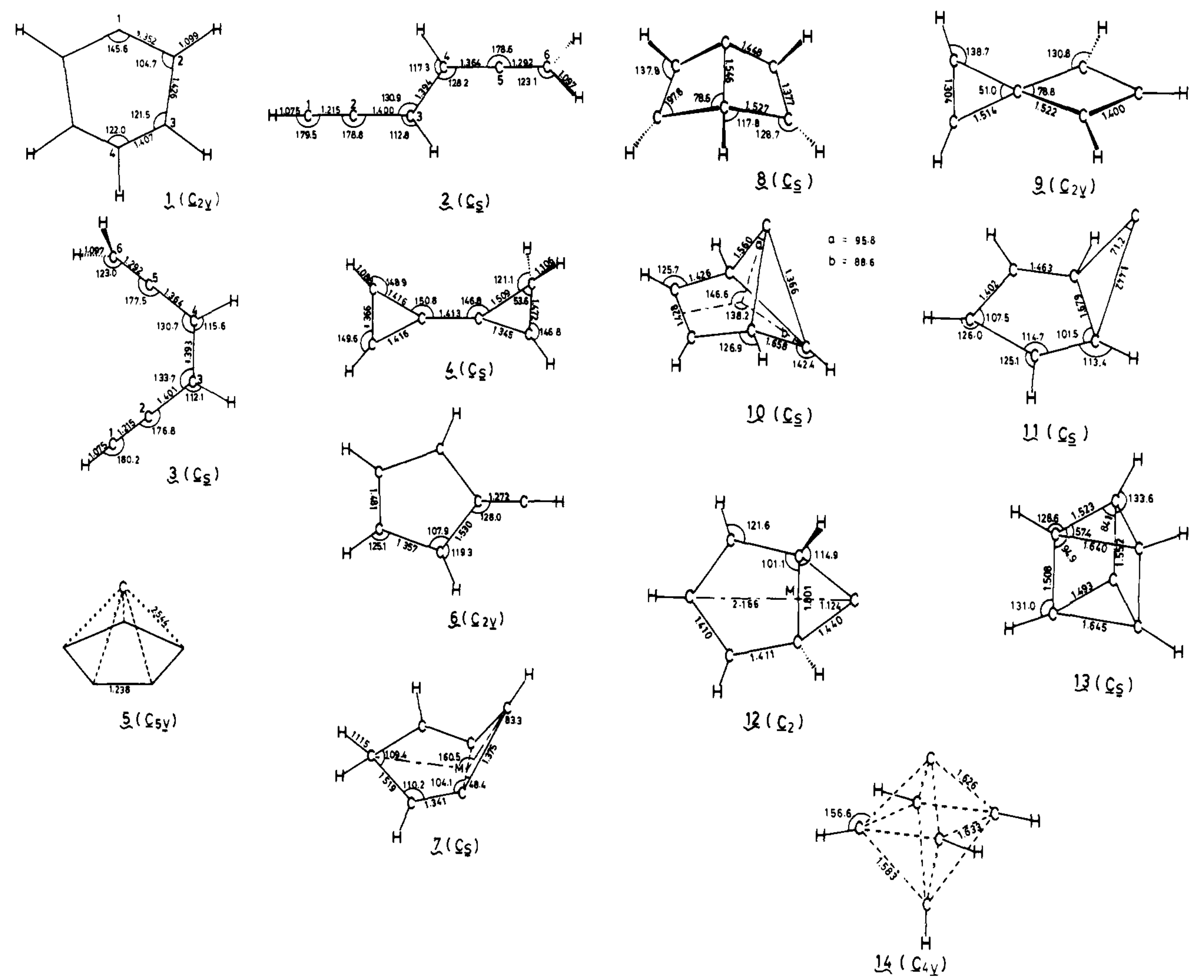

Figure 1. Theoretical structures of $C_6H_5^+$ by MINDO/3. Bond lengths and bond angles are shown in Å and deg, respectively.

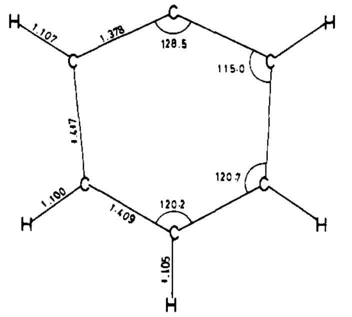

Figure 2. The theoretical structure of the phenyl radical by MINDO/3 with the "half-electron" method.[18]

perimental and calculated values are compared.[19] The heat of formation for the phenyl radical thus obtained is 76.1 kcal/mol. Since the ionization potential of the phenyl radical is 8.1 eV,[20] the calculated vertical heat of formation is 262 kcal/mol which is in good agreement with the value of 266 kcal/mol by the vertical process.[16]

Figure 3 shows the geometrical structures of the most stable $C_6H_5^+$ ion by the ab initio STO-3G and 6-31G[21] methods. Figures

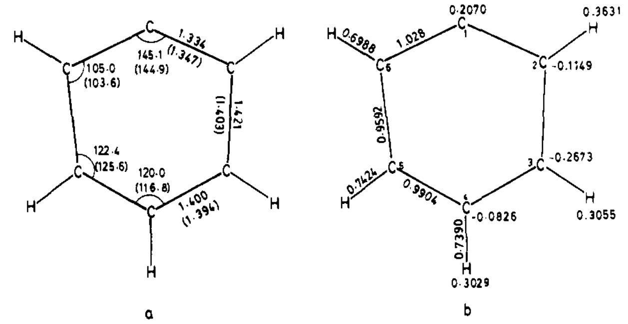

Figure 3. Ab initio calculations on the ground-state phenyl cation. (a) Bond lengths (in Å) and bond angles (in deg) calculated by 6-31G or STO-3G (in parentheses). The results by STO-3G were quoted from the literature.[8] (b) Gross atomic and bond populations by 6-31G.

1 and 3 show that STO-3G, 6-31G, and MINDO/3 methods give similar theoretical structures. Interestingly the structure by MINDO/3 is very close to that by 6-31G rather than STO-3G, suggesting appropriateness of adopting MINDO/3 for the calculation of ions. Since similar discussions made by Dill et al.[8] can be applied to this result, further comment is not made here except for the fact that the large bond population of C_1–C_2 and small ones of C_2–C_3 and C_2–H support the σ-type hyperconjugation between the formal vacant orbital at C_1 and the bonds C_2–C_3, C_2–H, etc., and also indicate easy cleavage of those bonds.

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[19] Some papers have compared the calculated heats of formation with the vertical heats of formation for appreciation of the MO methods used there (e.g., Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1294). Such a comparison is valid only when the most stable geometries of the radical and the cation are similar, but generally it is erroneous.

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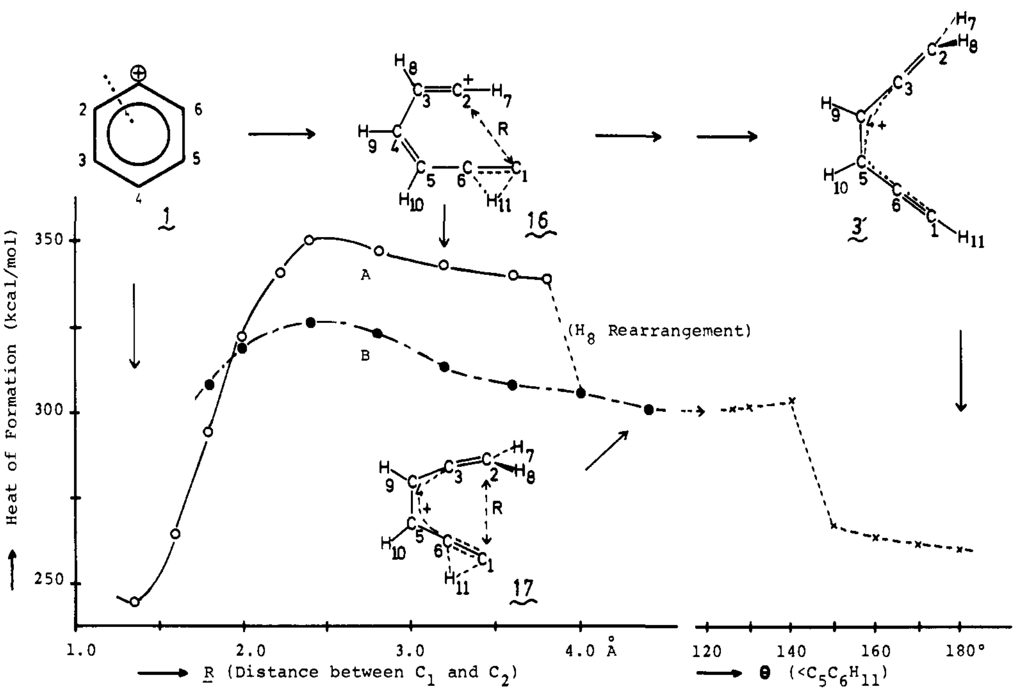
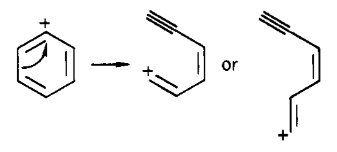


Figure 4. Potential energy curves for the α-bond cleavage of the ground-state phenyl cation.

Figure 1 also shows the theoretical structures of the other isomers. Since the previous calculation by MINDO/3[10] neglects the optimization concerning the C–H bonds, our results appear lower in heats of formation, especially in structures **4** and **13**. Complete scrambling on the carbon atoms has been observed in the fragmentation of benzene. In order to explain it, such intermediate isomers as prizmane and benzvalene are proposed[22] by analogy with photochemical transformations.[23] Unlike the benzene ion, the phenyl cation has less probability for such structures because of the instability of those ions.

The second most stable structure is **2**. At first we supposed that scission of the β band to the cation center (C_1) (that corresponds to the β-bond cleavage once defined by McLafferty[24]) might give a stable isomer (**15** in eq 2), which was used as the


(2)

15

initial geometry and allowed to be optimized, automatically giving the final structure **3**, the cis isomer of **2**; there is no potential barrier when the hydrogen atom attached to C_5 moves to C_6.

Formally C_1 or C_5 in both **2** and **3** are the cation centers with a vacant p orbital which conjugates with the π bonds. The total energy (E) calculated by the MO theories which neglect three- and four-center interactions can be expressed as the sum of one- and two-center terms

$$E = \sum E_A + \sum_{A>B} E_{AB} \tag{3}$$

The two-center terms (E_{AB}'s) are shown to serve as a good estimate of the strength of the covalent bond between atoms A and B.[25] In both **2** and **3**, the calculated E_{AB} values are almost the same for corresponding bonds, within a difference of 1 kcal/mol. Using E_{AB} values, the bonds C_2–C_3, C_3–C_4, and C_4–C_5 were found to be weak (−19.5, −20.8, and −21.7 eV, respectively) when compared to the bonds C_1–C_2 and C_5–C_6 (−33.2 and −26.6 eV, respectively), indicating that the bonds were broken. Other electronic structures (the electron densities, bond orders, and the contribution of each atomic orbital to E_A and E_{AB}[25]) are nearly the same between **2** and **3**. The activation energy of geometrical conversion **2** → **3** (and also **3** → **2**) is calculated to be as low as 12 kcal/mol. Therefore, those ions are considered to behave similarly in the fragmentation. As already pointed out,[10] the ligand-type structure **5** is interestingly stable; this isomer might possibly be the intermediate of scrambling of carbon atoms in **1**. The details on this respect will be discussed later.

Potential Energies Involved in the Fragmentation from the Stable $C_6H_5^+$ Ions. The $C_6H_5^+$ ions are well-known to give the $C_4H_3^+$ ion with loss of C_2H_2. Such a fragmentation could occur from the isomers with high heat of formation. However, we do not take them into account, assuming that ions with low energy are more abundantly formed than those with high energy. This might be supported by the fact that most fragmentations favor the cleavages that give stable products.[2] We will examine ions **1**–**3** in this paper.

Figure 4 displays the potential energies for the α-bond cleavage, where optimization for all geometrical parameters except the reaction coordinate was carried out. The α-bond cleavage involves various structures such as **16**, **17**, and those between **1** and **16**, **17** and **3'**, etc. The reaction coordinate shown by R represents the distance between C_1 and C_2 of **1**, **16**, or **17**, while θ is the angle between C_5 and H_{11} at C_6 in **17**. Elongation of R in **1** gives the potential energy curve indicated by A. The structure **16** is an approximate geometry of A with R being ca. 3 Å. At the distance when R is 3.8 Å, H_8 migrates from C_3 to C_2 giving a structure such as **17**, which has another series of potential energies (B) concerning the distance between C_1 and C_2. At first the reaction may proceed on the potential surface of A. However, it is probable that if, before the system reaches the peak of A, the migration of H_8 involves lower potential energies than that at the peak (ca. 350 kcal/mol in heat of formation), such a migration may precede. Therefore, in order to obtain the minimum energy reaction path (MERP) for the α-bond cleavage, we examined the potential energies of the H_8 migration at several values of R; the MERP for H_8 migration is found when R is 1.8 Å, where the highest heat of formation is 328 kcal/mol. Thus the activation energy for the α-bond cleavage is predicted to be 83 kcal/mol. The potential energies as a function of θ in Figure 4 show that the ion **17** possibly changes to **3** without any remarkable activation energy. One may

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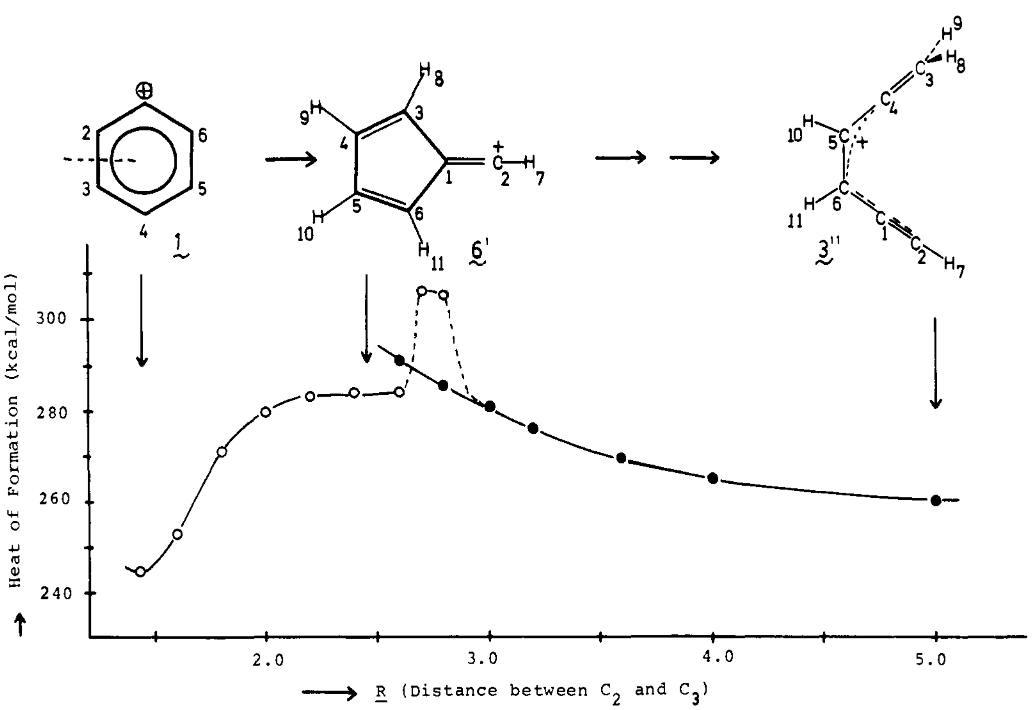


Figure 5. Potential energy curve for the β-bond cleavage of the ground-state phenyl cation.

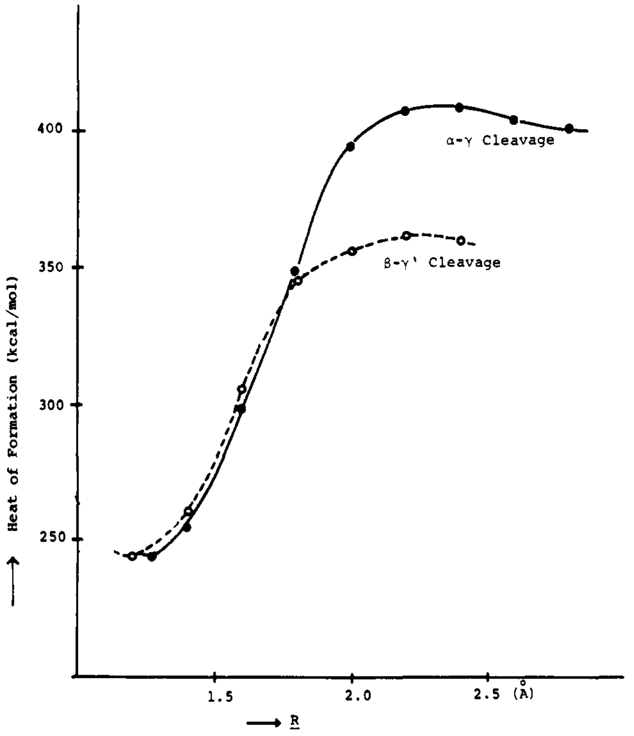


Figure 6. Potential energy curves for simultaneous two-bond cleavages in the ground-state phenyl cation.

consider that much lower MERP could be found if the structure **3** is used in place of **17** which has been used for curve B. The potential energies by such a procedure are, in fact, those for the β-bond cleavage.

In Figure 5 are the potential energies for the β-bond cleavage obtained by a procedure similar to that in Figure 4. Where the reaction coordinate R, the distance between C_2 and C_3 in **1**, is between 2.0 and 2.6 Å, the system is on a plateau of potential energy on which the fulvene structure (**6'**) is maintained. Where R is between 2.6 and 2.7 Å, a steep increase of potential energy appears by the bond breaking of C_1–C_3 of **6'**, while abrupt decrease around R = 2.8 Å is brought forth by the rearrangement of H_9 from C_4 to C_3. The highest heat of formation of this process is 307 kcal/mol. To obtain the MERP for the β-bond cleavage, the hydrogen migration (H_9) has been examined at several points of R with results that indicate such a migration is unfavorable since the calculated heat of formation exceeds 307 kcal/mol at any point. The theoretical activation energy for the β-bond cleavage is thus determined as 62 kcal/mol.

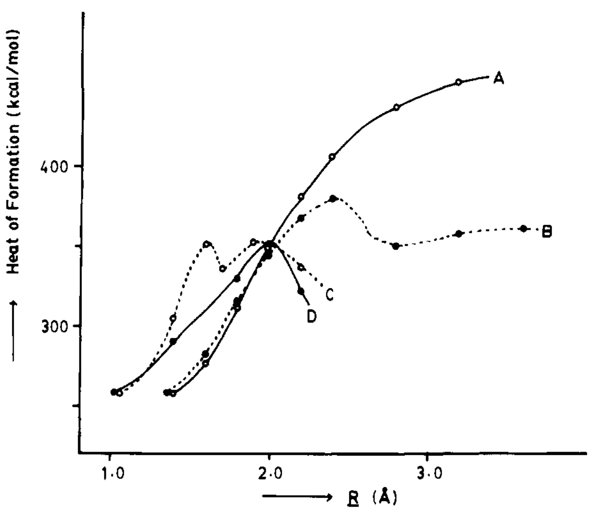
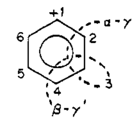


Figure 7. Potential energy curves for the fragmentations from **2** and **3**. A and B are the results for the bond-scissions of C_2–C_3 and C_4–C_5 in **2**, respectively, while C and D are those which pass through cyclic transition states in **2** and **3**, respectively.

Simultaneous Cleavage of Two Bonds in 1. We next considered the cases when the phenyl cation loses C_2H_2 by simultaneous two-bond scission, α–γ and β–γ' cleavages shown below.



The case in which the leaving C_2H_2 molecule includes the C_1 atom was not taken into account. Figure 6 shows the potential energies for such cases where the reaction coordinate R is defined as the distance between the centers of C_2H_2 and the line that connects C_1 and C_4 (in the α–γ cleavage) or C_2 and C_5 (in the β–γ'

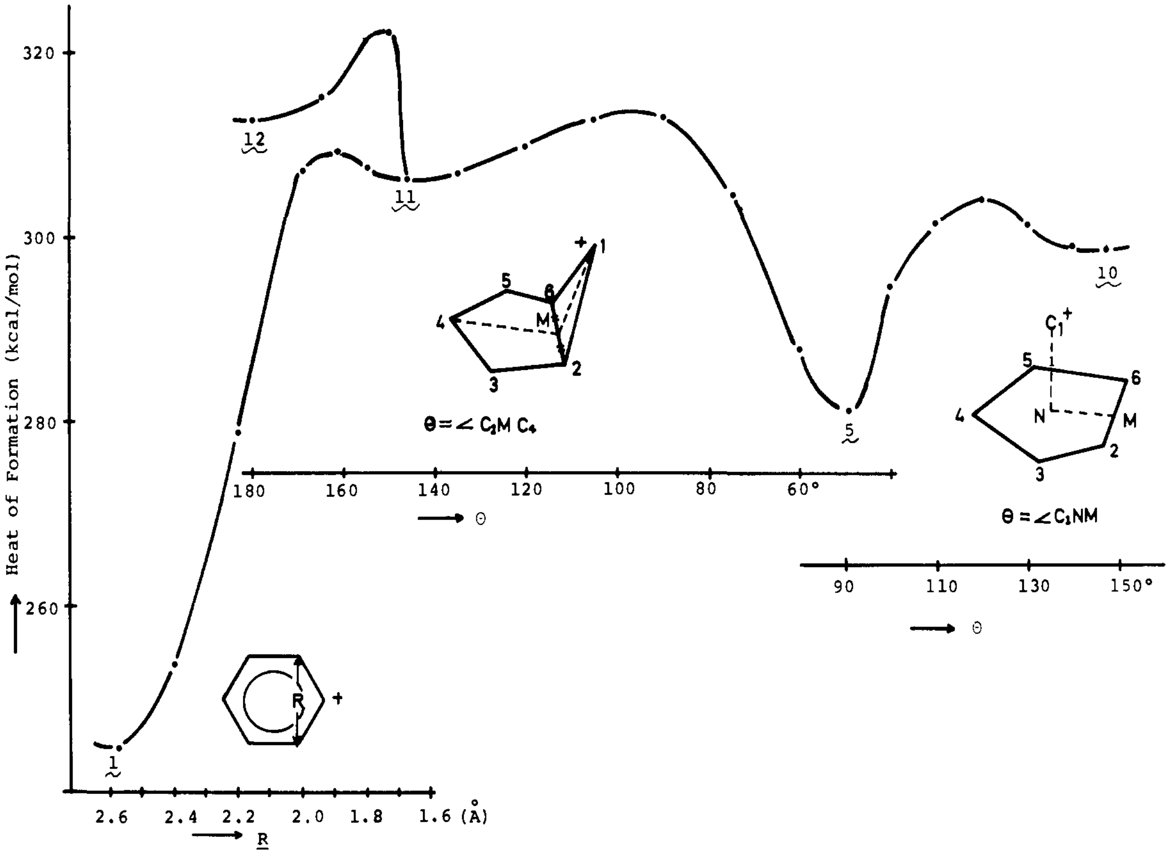
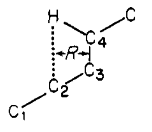


Figure 8. Potential energy curves for **1** → **11**, **11** → **12**, **11** → **5**, and **5** → **10**.

cleavage); all other geometrical parameters are optimized. Increase of potential energy is monotonous in spite of substantial changes of geometry; at the highest potential energy of the α–γ cleavage the C_4H_3 fraction has a nonclassical structure. The activation energies of the α–γ and β–γ' cleavages are 163 and 118 kcal/mol, respectively. This result is favorable for the fragmentation rules in that the cleavage involving the β bond has the lower activation energy.

Fragmentations from 2 and 3. Two probable fragmentations which discharge C_2H_2 from **2** and **3** are the bond scissions of C_4–C_5 or C_2–C_3. In the latter cleavage C_2 must be accompanied by a hydrogen atom in the fragmentation. Figure 7 displays the heats of formation as functions of R, the distance between C_2 and C_3 (A) or C_4 and C_5 (B). The cleavage of C_4–C_5 brings forth lower potential energies than that of C_2–C_3. However, since the elongation of C_2–C_3 did not cause C_2 to attract the hydrogen atom attached to C_4, we examined the cyclic transition states which are composed of C_2, C_3, C_4, and H or C_5. The potential energies were calculated as functions of the distance R between the centers of C_3–C_4 and C_2–H in **2** (C) or C_3–C_4 and C_2–C_5 in **3** (D) and are shown in Figure 7. The highest potential energy thus obtained



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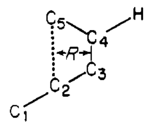

3

is 353 kcal/mol in both cases. Therefore, the activation energies for the fragmentation from **1** and **2** or **3** are ca. 108 and 93 kcal/mol, respectively. The activation energy of the cyclic transition state is lower than that of the acylic one (122 kcal/mol). Concerning this, the symmetry conservation rules have been applied to the interpretation of mass spectral fragmentation.[26] However, the rules are not as obvious as in the neutral molecule with even number of electrons. For example, the reaction which passes through a four-membered transition state is a symmetry forbidden reaction where the high transition energy is caused by the electrons in the HOMO. The problem is, however, that there is a large possibility that in the electron deficient system the HOMO is not doubly occupied to reduce such a high transition energy. Our results concerning the fragmentations of **2** and **3** may be examples showing that the concept of symmetry controlled reaction is not always true in the electron deficient system.

The lowest activation energy for the phenyl cation to release C_2H_2 is thus calculated to be 108 kcal/mol. Hydrogen chemical ionization (H_2 CI) of fluoro- or chlorobenzene produces abundant phenyl cation, which is, however, known not to release C_2H_2.[27] This may be explained as follows: since the observed proton affinities of H_2, fluorobenzene, and chlorobenzene are 105,[28] 182,[29] and 182 kcal/mol,[29] respectively, the internal energy given by the protonation on those compounds is ca. 77 kcal/mol. Suppose that the phenyl cation produced from the protonated halobenzene has a heat of formation of ca. 270 kcal/mol, 25 kcal/mol higher than the calculated ground-state structure, then the internal energy of the phenyl cation thus formed is predicted to be 102 kcal/mol at most. Since the release of HX (X = F or Cl) may reduce the internal energy of the system causing the internal energy of $C_6H_5^+$ to be lower than 102 kcal/mol, it may be too low to pass through a transition state during the fragmentation of the ion.

Potential Energies for the Scrambling of Carbon and Hydrogen Atoms in Phenyl Cation. Successive mutual conversions between **1** and **6** would lead to complete randomization of carbon atoms in **1**. In this case the activation energy is 40 kcal/mol. However, the unexpected stable structure for **5** has encouraged us to calculate the potential energies for **1** → **5**. The structure **5** seems to be an appropriate intermediate of complete scrambling of carbon atoms, since it has a high number of symmetry (C_{5v}); the reverse reaction (i.e., **5** → **1**) means the complete randomization of carbon atoms in **1**, independently of hydrogen scrambling. The results are shown

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Table II. Activation Energies for Interstructural Conversions in the $C_6H_5^+$ System (kcal/mol)[a]

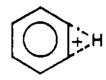
	1	2	3	5	6	10	11	12
1		62	62	69	40	69	65	78
2	47		13	54	25	54	50	63
3	46	12		53	24	53	49	62
5	32	32	32		32	23	32	41
6	1	1	1	29		25	25	38
10	14	14	14	5	14		14	23
11	3	3	3	7	3	7		16
12	10	10	10	10	10	10	10	

[a] The figures in the *i*th row show the activation energies for the structural conversion from the structure *i*, while those in the *j*th column express the conversion from the structure *j*. For example, the activation energy from **1** to **2** is read as 62 kcal/mol, whereas from **2** to **1** it is 47 kcal/mol.

in Figure 8 where the heats of formation are plotted against three different reaction coordinates; for **1** → **11** the reaction coordinate is the distance (*R*) between C_2 and C_6 in **1** for **12** → **5** and **5** → **10**, the reaction coordinate is the angle (θ) of C_1 in the molecular plane (see **11** and **5** in Figure 8). The highest potential energy appears to be **11** → **5**—314 kcal/mol; the activation energy is, therefore, 69 kcal/mol. It should be stressed that this value and the activation energy for **1** → **6** are far lower than the energy required for fragmentation, indicating that the carbon atoms in the phenyl cation can be randomized prior to fragmentation.

It has been reported that before the loss of C_2H_2 from the $C_6H_5^+$ ion, which is produced from iodobenzene by electron impact, the six carbon and hydrogen atoms are completely randomized.[30] The heat of formation of $C_6H_5^+$ from iodobenzene has been measured to be 299 kcal/mol.[31] This value is 54 kcal/mol higher than that of the ground-state phenyl cation. Since most phenyl cations formed by electron impact have extra internal energy, the scrambling of the carbon atoms possibly occur even if they do not give rise to fragmentation.

A MINDO/3 calculation on structure **18** has been performed resulting in a heat of formation 44 kcal/mol higher than **1**.[8] This structure is considered to be the acceptable intermediate of hydrogen randomization, since the scrambling could proceed by successive 1,2 shifts. Although we further tried to find out the MERP under conditions that maintain the ring structure in **1**, there was no other path. Conclusively, the activation energy of hydrogen scrambling is lower than the energies for fragmentation and is comparable to that of carbon scrambling.



18

Conclusion

The stabilities of the $C_6H_5^+$ system are calculated as shown in Table I. The lowest activation energy for elimination of C_2H_2 from **1** is predicted to be 108 kcal/mol. This elimination should occur through a linear structure (either **2** or **3**), which may be formed by the β-bond cleavage of **1**. On the other hand, direct loss of C_2H_2 from **1** requires ca. 118 kcal/mol. Generally the cleavage involving the β bond to the carbon atom with the formal cation is easier than the α bond. These results support the concept of the fragmentation rules in the aromatic ring system.

The energies which are required for interstructural conversions are in Table II. Those values are relatively low when compared to the energies for fragmentation, suggesting easy mutual conversion before fragmentation. The possible least energy path for 1 → 5, one of the paths of carbon scrambling, is examined to give 69 kcal/mol above 1. This value is far lower than that of fragmentation, explaining the experimental results of the phenyl cation produced from iodobenzene by electron impact. Ease or difficulity of hydrogen migration between carbon atoms entirely depends on the structure of the ion, although hydrogen scrambling in **1** needs 44 kcal/mol.

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Evaluation and Prediction of the Stability of Bridgehead Olefins[1]

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Abstract: Geometries, heats of formation, heats of hydrogenation, and strain energies of bridgehead olefins and the related polycycloalkanes have been calculated by using Allinger's MM1 empirical force field program. The "olefin strain" energy (OS), defined as the difference between the strain energy of an olefin and that of its parent hydrocarbon, can be used to interpret and to predict the stability and the reactivity of bridgehead olefins. A new class of compounds has been recognized, the "hyperstable" olefins, which are *less* strained than the parent hydrocarbon and should show *decreased reactivity* because of the bridgehead location of the double bonds.

Since 1924,[2] when Bredt pointed out that double bonds tend to avoid ring junctions in camphane and pinane systems, bridgehead olefins have received special and increasing attention.[3-5] What are the limits of applicability of Bredt's rule? Extensive experimental work especially during the last decade has necessitated one refinement after another. The first systematic study by Prelog[6] on bicyclo[*X*.3.1]alkenones indicated that *X* = 5

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