Theoretical Approach for the Equilibrium Structures and Relative Energies of $C_7H_7^+$ Isomers and the Transition States between *o-*, *m-*, and *p*-Tolyl Cations

Chang-Ho Shin, Kyung-chun Park, Seung-Joon Kim,[*] **and Byungjoo Kim**[†]

Department of Chemistry, HanNam University, Taejon 300-791, Korea
[†]*Division of Chemical Metrology and Materials Evaluation, Korea Research Institute of Standards and Science*
P.O. 102, Yusong, Taejon 305-600, Korea

The equilibrium structures for the ground and transition states of $C_7H_7^+$ isomers have been investigated using sophisticated *ab initio* quantum mechanical techniques with various basis sets. The structures of tropyrium and benzyl cations have been fully optimized at the DZP CCSD(T) levels of theory. And the structures of *o-*, *m-* and *p*-tolyl cations are optimized fully up to the DZ CCSD(T) levels of theory. The geometries for the transition states between three isomers of tolyl cations have been optimized up to DZP CISD level of theory. The SCF harmonic vibrational frequencies for tropylium, benzyl, and three isomers of tolyl cations are all real numbers, which confirm the potential minima and each unique imaginary vibrational frequencies for **TS1** and **TS2** confirm the true transition states. The relative energy of the benzyl cation with respect to the tropyrium cation is predicted to be 28.5 kJ/mol and is in good agreement with the previous theoretical predictions. The 0 K heats of formation, ΔH_{f0}°, have been predicted to be 890, 1095, 1101, and 1110 kJ/mol for tropylium, *ortho-*, *meta-*, and *para*-tolyl cations by taking the experimental value of 919 kJ/mol for the benzyl cation as the base level. The relative stability between tolyl cations is in the order of *ortho* < *meta* < *para* and is in good agreement with previous theoretical predictions both in magnitude and in order. The energy barriers are predicted to be 51.2 kcal/mol for the rearrangement from *o*-tolyl to *m*-tolyl cation and 53.1 kcal/mol for conversion of *m*-tolyl cation to *p*-toly.

Keywords : *Ab initio*, $C_7H_7^+$, Tolyl, Benzyl, Tropylium.

Introduction

The formation of $C_7H_7^+$ ion from the dissociations of halotoluene radical cations ($C_7H_7X^+$) has been one of the most interesting and challenging reactions to be studied in mass spectrometry. Earlier studies focused on the structure of $C_7H_7^+$ products and the kinetics of the unimolecular dissociations.[1-11] Those reactions have been known to have two competing pathways[1-9] and the structures of $C_7H_7^+$ products have been known to be benzyl, tropylium, and tolyl cations.[5,6,10-13] The widely accepted two channel mechanisms include direct C-X bond cleavage channel I leading to the formation of the tolyl ions and lower energy barrier channel II which leads to the formation of either the benzyl cations or tropylium cations or both.[1-8] However, the energetics and mechanisms of the structural rearrangements of $C_7H_7^+$ product ions following the formation of the ions have not been well established,[10-13] which has made it difficult to draw well-establish picture of the two-channel mechanisms even with such extensive experimental studies. Most recently, the structure of $C_7H_7^+$ ion from channel II was identified as the benzyl cation from the product-resolved spectroscopy following the energy-selective photodissociation of bromotoluene radical cations.[5,6] This study also proved that the tropylium cations results mostly from the rearrangements of tolyl cations formed from channel I. The results emphasized that the establishment of the energetics of $C_7H_7^+$ isomers and the rearrangement processes among the isomers are necessary to establish the dissociation mechanisms of halotoluene radical cations.

The heat of formation of the benzyl cation is relatively accurately known from the dissociative ionization studies of benzyl halide[14-16] and the ionization energy of the benzyl radical.[17-19] The heat of formations of three structural isomers of tolyl cations were reported by Lin and Dunbar[1] from the kinetic modeling based on their time-resolved photodissociation (TRPD) studies of iodotoluene radical cations and by Baer *et al.*[9] from the photoelectron-photoion coincidence (PEPICO) spectroscopic studies of *m-* and *p*-nitrotoluene radical cations. However, TRPD results and PEPICO results do not agree on the relative stability between *m-* and *p*-tolyl cations. Determination of the heat of formation of tropylium cation from such kinetic studies has been difficult due to the presence of reverse activation barriers in unimolecular dissociations leading to the tropylium cation in most of target molecular radical cations and there was little agreement among several experimental results.[12,16,20] For a long time, only theoretical calculations reported by Dewar *et al.* using low level MINDO[21] has been available as complementary information to experimental results. In 1994, Nicolaides and Radom reported the relative energy between benzyl and tropyrium cations using G2 calculation.[22] Also, MP4 relative energies of benzyl, tropylium, *o-*, *m-*, and *p*-tolyl cations were reported in 1997 by Shin.[23] However the energy barrier for the rearrangement between tolyl cations using high level *ab initio* algorithm has not been available until Ignatyev and

Sundius reported their DFT results in 2000.[24]

To help establish the energetics of the $C_7H_7^+$ isomers and the rearrangement mechanisms between the isomers, high level *ab initio* calculations were performed. The geometry optimizations were carried out at the DZP CCSD(T) level of theory for the tropylium and benzyl cations, at the DZ CCSD(T) level of theory for the *o-*, *m-*, *p*-tolyl cations, and at the DZP CISD level of theory for the transition states between three tolyl cation isomers. The SCF harmonic vibrational frequencies and zero-point vibrational energies (ZPVEs) at the equilibrium geometries of the $C_7H_7^+$ isomers were also evaluated to obtain their relative energies. Herein, we report the relative energies for the potential minima of $C_7H_7^+$ isomers and the energy barriers for the rearrangements between *o-*, *m-*, and *p*-tolyl cations.

Theoretical Approach

The basis sets used in this study are of double zeta (DZ), DZ plus polarization (DZP), and triple zeta plus polarization (TZP) quality. The DZ basis set consists of the standard Huzinaga[25] and Dunning[26] (9s5p/4s2p) contracted Gaussian functions for carbon and oxygen and the (4s/2s) set for hydrogen. The DZP basis is DZ plus a single set of polarization *d* functions on carbon and oxygen, and a set of *p* functions on hydrogen with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_p(H) = 0.75$. The TZP basis is of triple zeta (TZ) quality with one set of polarization function (orbital exponents are the same with DZP), while the TZ basis consists of the Huzinaga[25] and Dunning[27] (10s6p/5s3p) set for C and the (5s/3s) set for H. The numbers of basis functions are 84, 147, and 182 with the DZ, DZP, and TZP basis sets.

The geometries of the $C_7H_7^+$ isomers and the transitions states are fully optimized at the self-consistent field (SCF) level of theory using analytic technique[28] with DZ, DZP, and TZP basis sets. The SCF equilibrium geometries are sub-sequently used as starting points to optimize structures at the single and double excited configuration (CISD) level with DZ and DZP basis sets described above employing analytic CISD gradient methods.[29] The CISD geometries of the $C_7H_7^+$ isomers are finally used to obtain geometries optimized at the CCSD levels, which is the single and double excitation coupled cluster method. And the single point energy at CCSD optimized geometry has been performed at CCSD(T) level of theory, which is consisted of CCSD with the effects of connected triple excitations included perturbatively.[30] In the CISD, CCSD, and CCSD(T) wavefunctions, the seven core-like occupied SCF molecular orbitals are frozen (held doubly occupied) and the seven highest virtual molecular orbitals are deleted from the correlation procedures. With the DZP basis set, the CISD wave functions include 1,232,860 configurations in C_{2v} symmetry, 2,375,569 configurations in C_s symmetry, and 4,361,581 configurations in C_1 symmetry.

Harmonic vibrational frequencies and ZPVEs for the equilibrium geometries of $C_7H_7^+$ isomers are evaluated using analytic second energy derivatives[31] at the SCF level. All computations described above are carried out with the PSI-2[32] suite of computer programs developed in professor Schaefer's laboratory.

Results and Discussion

Geometries. The geometry of the tropylium cation optimized at the DZP CCSD(T) level of theory has been shown in Figure 1(a), and the geometrical parameters at other levels of theory are listed in Table 1. This seven-membered ring which is in the D_{7h} symmetry has the same C-C and C-H bond distances of 1.410 and 1.092 Å. These results are slightly longer than those (1.396 and 1.082 Å)[33] of benzene. As shown in Table 1, the electron correlation effect increases the bond lengths for both C-C and C-H as usual and the basis set effect decreases bond distances in going from DZ to DZP
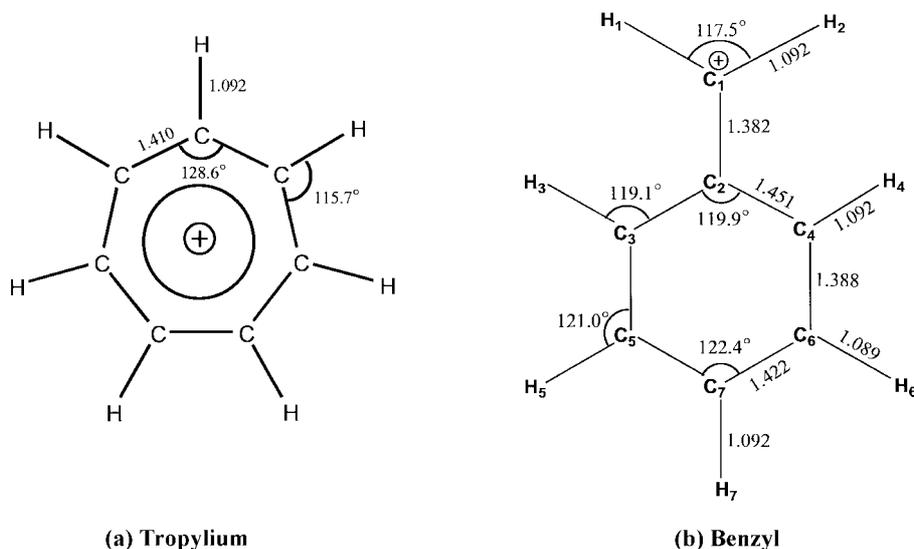

(a) Tropylium   **(b) Benzyl**

Figure 1. Predicted geometries for the (a) tropylium and (b) benzyl cations at the DZP CCSD(T) level of theory. Bond lengths are in Å and bond angles are in degrees.

Table 1. Geometrical parameters of the tropylium cation at various levels of theory

	SCF			CISD		CCSD		CCSD(T)	
	DZ	DZP	TZP	DZ	DZP	DZ	DZP	DZ	DZP
R(C-C)	1.397	1.393	1.386	1.411	1.394	1.426	1.406	1.430	1.410
R(C-H)	1.073	1.077	1.075	1.086	1.081	1.097	1.090	1.099	1.092
∠(CCH)	115.7	115.7	115.7	115.7	115.7	115.7	115.7	115.7	115.7
∠(CCC)	128.6	128.6	128.6	128.6	128.6	128.6	128.6	128.6	128.6

Bond lengths are in Å and bond angles are in degrees.

Table 2. Geometrical parameters of the benzyl cation at various levels of theory

	SCF			CISD		CCSD		CCSD(T)	
	DZ	DZP	TZP	DZ	DZP	DZ	DZP	DZ	DZP
$R(C_1-H_1)$	1.074	1.078	1.076	1.087	1.081	1.098	1.090	1.099	1.092
$R(C_1-C_2)$	1.369	1.361	1.355	1.381	1.363	1.395	1.376	1.401	1.382
$R(C_2-C_4)$	1.441	1.438	1.434	1.455	1.436	1.470	1.448	1.474	1.451
$R(C_4-C_6)$	1.373	1.366	1.359	1.387	1.369	1.403	1.383	1.408	1.388
$R(C_6-C_7)$	1.411	1.407	1.400	1.424	1.406	1.439	1.418	1.443	1.422
$R(C_4-H_4)$	1.073	1.077	1.075	1.085	1.080	1.096	1.090	1.098	1.092
$R(C_6-H_6)$	1.069	1.075	1.073	1.082	1.078	1.093	1.087	1.095	1.089
$R(C_7-H_7)$	1.072	1.078	1.076	1.085	1.081	1.097	1.091	1.098	1.092
$\theta(H_1C_1H_2)$	116.5	117.0	116.8	116.7	117.1	116.8	117.3	116.9	117.5
$\theta(C_2C_3H_3)$	119.3	119.1	119.1	119.1	119.2	119.1	119.1	119.0	119.1
$\theta(C_3C_5H_5)$	120.9	121.2	121.1	120.9	121.1	120.9	121.0	120.8	121.0
$\theta(C_3C_2C_4)$	118.9	119.2	119.1	119.2	119.6	119.3	119.7	119.4	119.9
$\theta(C_5C_7C_6)$	122.2	122.7	122.8	122.2	122.7	122.1	122.5	122.0	122.4

Bond lengths are in Å and bond angles are in degrees.

or TZP. The predicted geometry (C_{2v} symmetry) of benzyl cation appears in Figure 1(b) and structural parameters at various levels of theory are listed in Table 2. For the benzyl cation, the electron correlation effect increases bond distances significantly going from SCF to CISD or from CISD to CCSD, while the change between CCSD and CCSD(T) level of theory is not too serious. The bond distances decrease with increasing the basis set size from DZ to DZP. The predicted bond length of C_1-C_2 at the DZP CCSD(T) level of theory is 1.382 Å, which has slightly more π character than
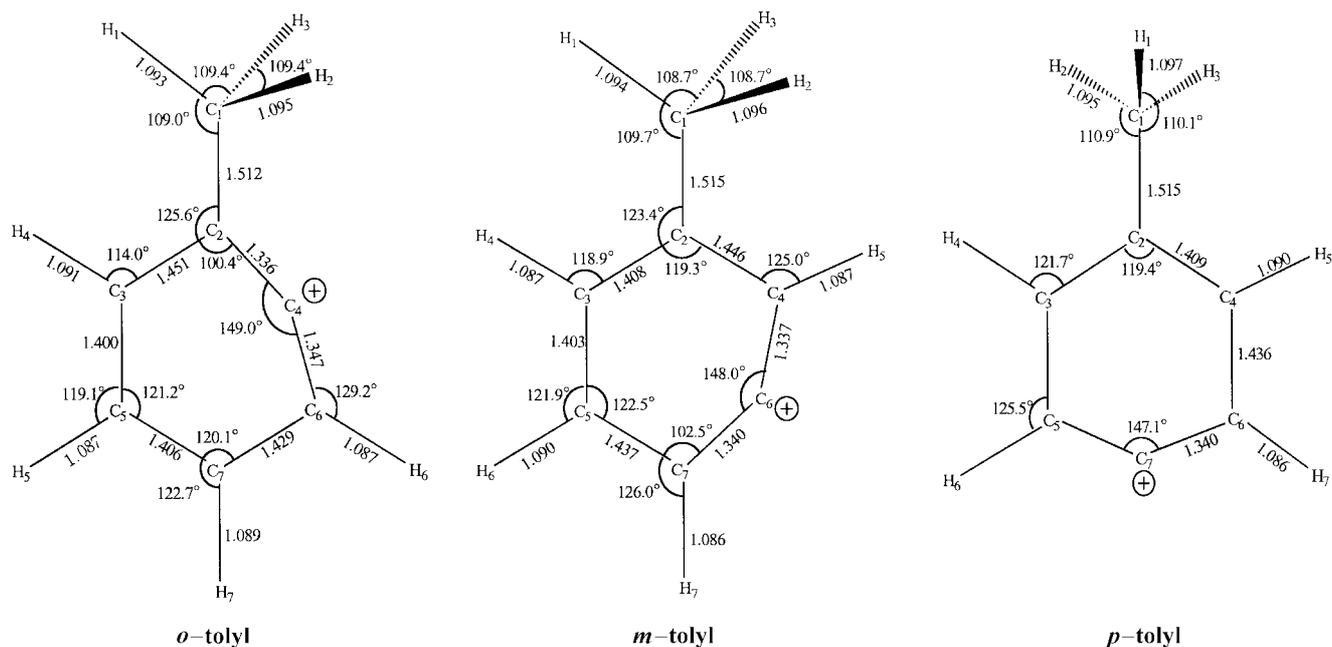

Figure 2. Predicted geometries for the *o*-, *m*-, and *p*-tolyl cations at the DZP CCSD level of theory. Bond lengths are in Å and bond angles are in degrees.

Table 3. Geometrical parameters of the *o*-tolyl cation at various levels of theory

	SCF			CISD		CCSD		CCSD(T)
	DZ	DZP	TZP	DZ	DZP	DZ	DZP	DZ
R(C$_1$-H$_1$)	1.078	1.081	1.079	1.091	1.083	1.103	1.093	1.104
R(C$_1$-H$_2$)	1.081	1.084	1.082	1.093	1.085	1.105	1.095	1.106
R(C$_1$-C$_2$)	1.513	1.510	1.506	1.523	1.503	1.537	1.512	1.540
R(C$_2$-C$_3$)	1.433	1.428	1.425	1.456	1.433	1.479	1.451	1.488
R(C$_2$-C$_4$)	1.340	1.327	1.318	1.346	1.326	1.357	1.336	1.360
R(C$_3$-C$_5$)	1.397	1.389	1.382	1.408	1.389	1.421	1.400	1.425
R(C$_4$-C$_6$)	1.346	1.338	1.328	1.353	1.336	1.367	1.347	1.369
R(C$_5$-C$_7$)	1.403	1.396	1.390	1.414	1.395	1.428	1.406	1.430
R(C$_6$-C$_7$)	1.415	1.407	1.402	1.436	1.413	1.456	1.429	1.464
R(C$_3$-H$_4$)	1.071	1.078	1.075	1.085	1.081	1.096	1.091	1.099
R(C$_5$-H$_5$)	1.069	1.075	1.073	1.082	1.078	1.093	1.087	1.095
R(C$_6$-H$_6$)	1.069	1.075	1.072	1.081	1.077	1.092	1.087	1.093
R(C$_7$-H$_7$)	1.070	1.076	1.074	1.083	1.079	1.094	1.089	1.096
∠ (H$_1$C$_1$H$_3$)	108.7	109.2	109.2	108.9	109.2	109.1	109.4	109.2
∠ (H$_2$C$_1$H$_3$)	108.8	109.2	109.2	109.0	109.2	109.2	109.4	109.3
∠ (C$_2$C$_1$H$_1$)	109.4	109.1	109.1	109.2	109.1	109.0	109.0	109.0
∠ (C$_1$C$_2$C$_3$)	125.8	126.6	126.5	125.3	126.1	124.8	125.6	124.5
∠ (C$_2$C$_4$C$_6$)	145.9	148.5	148.6	146.8	149.2	146.7	147.0	146.6
∠ (C$_3$C$_2$C$_4$)	103.1	101.2	101.2	102.4	100.4	102.5	100.4	102.4
∠ (C$_3$C$_5$C$_7$)	122.0	121.7	121.6	121.6	121.3	121.6	121.2	121.5
∠ (C$_5$C$_7$C$_6$)	120.1	120.2	120.1	120.2	120.2	120.1	120.1	120.0
∠ (C$_2$C$_3$H$_4$)	116.5	115.8	115.7	115.4	114.7	114.7	114.0	114.2
∠ (C$_3$C$_5$H$_5$)	118.8	118.9	119.0	119.0	119.1	119.0	119.1	119.0
∠ (C$_4$C$_6$H$_6$)	128.6	128.6	128.6	129.3	129.1	129.5	129.2	129.6
∠ (C$_5$C$_7$H$_7$)	121.7	121.8	121.8	122.3	122.2	122.8	122.7	123.1

Bond lengths are in Å and bond angles are in degrees.

Table 4. Geometrical parameters of the *m*-tolyl cation at various levels of theory

	SCF			CISD		CCSD		CCSD(T)
	DZ	DZP	TZP	DZ	DZP	DZ	DZP	DZ
R(C$_1$-H$_1$)	1.080	1.083	1.081	1.093	1.084	1.105	1.094	1.106
R(C$_1$-H$_2$)	1.082	1.085	1.082	1.095	1.087	1.106	1.096	1.107
R(C$_1$-C$_2$)	1.513	1.512	1.509	1.524	1.505	1.539	1.515	1.542
R(C$_2$-C$_3$)	1.406	1.399	1.394	1.417	1.398	1.430	1.408	1.433
R(C$_2$-C$_4$)	1.430	1.424	1.419	1.452	1.428	1.475	1.446	1.485
R(C$_3$-C$_5$)	1.399	1.392	1.384	1.410	1.391	1.425	1.403	1.427
R(C$_4$-C$_6$)	1.338	1.328	1.320	1.345	1.327	1.356	1.337	1.358
R(C$_5$-C$_7$)	1.423	1.417	1.414	1.443	1.422	1.463	1.437	1.471
R(C$_6$-C$_7$)	1.339	1.328	1.317	1.347	1.327	1.361	1.340	1.364
R(C$_3$-H$_4$)	1.069	1.075	1.073	1.082	1.078	1.093	1.087	1.095
R(C$_4$-H$_5$)	1.070	1.075	1.072	1.081	1.078	1.092	1.087	1.094
R(C$_5$-H$_6$)	1.070	1.077	1.075	1.083	1.080	1.095	1.090	1.097
R(C$_7$-H$_7$)	1.069	1.074	1.071	1.080	1.077	1.091	1.086	1.092
∠ (H$_1$C$_1$H$_3$)	108.1	108.6	108.5	108.3	108.6	108.4	108.7	108.5
∠ (H$_2$C$_1$H$_3$)	108.2	108.5	108.5	108.5	108.5	108.7	108.7	108.8
∠ (C$_2$C$_1$H$_1$)	110.6	110.3	110.2	110.1	110.1	109.6	109.7	109.3
∠ (C$_1$C$_2$C$_3$)	122.7	122.7	122.7	123.1	123.0	123.7	123.4	124.1
∠ (C$_3$C$_2$C$_4$)	118.8	119.0	119.0	119.0	119.2	119.0	119.3	119.1
∠ (C$_3$C$_5$C$_7$)	121.7	122.3	122.2	121.9	122.6	121.8	122.5	121.7
∠ (C$_4$C$_6$C$_7$)	145.1	147.7	147.8	145.9	148.3	145.6	148.0	145.5
∠ (C$_5$C$_7$C$_6$)	104.5	102.8	102.8	104.1	102.2	104.4	102.5	104.6
∠ (C$_2$C$_3$H$_4$)	118.6	118.8	118.8	118.7	118.9	118.6	118.9	118.6
∠ (C$_2$C$_4$H$_5$)	124.6	125.9	125.8	124.1	125.5	123.5	125.0	123.1
∠ (C$_3$C$_5$H$_6$)	121.0	121.0	121.0	121.6	121.4	122.2	121.9	122.6
∠ (C$_5$C$_7$H$_7$)	125.4	126.6	126.4	125.1	126.3	124.7	126.0	124.3

Bond lengths are in Å and bond angles are in degrees.

Table 5. Geometrical parameters of the *p*-tolyl cation at various levels of theory

	SCF			CISD		CCSD		CCSD(T)
	DZ	DZP	TZP	DZ	DZP	DZ	DZP	DZ
$R(C_1-H_1)$	1.083	1.086	1.085	1.096	1.087	1.107	1.097	1.108
$R(C_1-H_2)$	1.081	1.083	1.082	1.093	1.085	1.105	1.095	1.106
$R(C_1-C_2)$	1.514	1.512	1.509	1.525	1.505	1.540	1.515	1.543
$R(C_2-C_4)$	1.407	1.399	1.394	1.418	1.398	1.431	1.409	1.434
$R(C_4-C_6)$	1.420	1.414	1.409	1.441	1.419	1.463	1.436	1.472
$R(C_6-C_7)$	1.340	1.330	1.320	1.348	1.328	1.360	1.340	1.362
$R(C_4-H_5)$	1.070	1.077	1.075	1.084	1.080	1.095	1.090	1.098
$R(C_6-H_7)$	1.069	1.075	1.071	1.080	1.077	1.091	1.086	1.093
$\angle(C_2C_1H_1)$	110.4	110.0	110.1	110.4	110.1	110.4	110.1	110.3
$\angle(C_2C_1H_2)$	111.2	110.9	111.0	111.1	111.0	110.9	110.9	110.8
$\angle(H_2C_1H_3)$	108.0	108.3	108.3	108.0	108.3	108.1	108.3	108.1
$\angle(C_3C_2C_4)$	120.0	119.7	119.5	119.7	119.4	119.7	119.4	119.7
$\angle(C_5C_7C_6)$	143.9	146.3	146.5	145.0	147.3	144.9	147.1	144.8
$\angle(C_2C_3H_4)$	120.9	120.9	120.9	121.3	121.2	121.9	121.7	122.3
$\angle(C_3C_5H_6)$	124.9	126.0	125.8	124.6	125.9	124.2	125.5	123.9

Bond lengths are in Å and bond angles are in degrees.

others. The C-C bond distances in six-membered ring show two long (1.451 Å and 1.422 Å for C_2-C_4 and C_6-C_7, respectively) and one short (1.388 Å for C_4-C_6). The bond angles are not affected too much by the electron correlation effect or the basis set size.

The optimized geometries for the *o*-, *m*-, and *p*-tolyl cations at the DZP CCSD level of theory are shown in Figure 2. DZP CCSD(T) calculations on the geometry optimizations for C_s symmetries (or C_1 symmetry) of $C_7H_7^+$ are too expensive (one point calculation for the Cs symmetry takes

about one month on the 43p model of IBM RS6000 workstation), therefore the single-point energy calculations without the geometry optimization at the DZP CCSD(T) level of theory have been performed on the *o*-, *m*- *p*-tolyl cations, which have C_s symmetries. To figure out the difference between CCSD and CCSD(T) geometries, full optimizations have been carried out at the DZ CCSD(T) level of theory, and the geometrical parameters of the *o*-, *m*-, and *p*-tolyl cations at various levels of theory are compared in Tables 3-5. From these results we found that the effects of connected
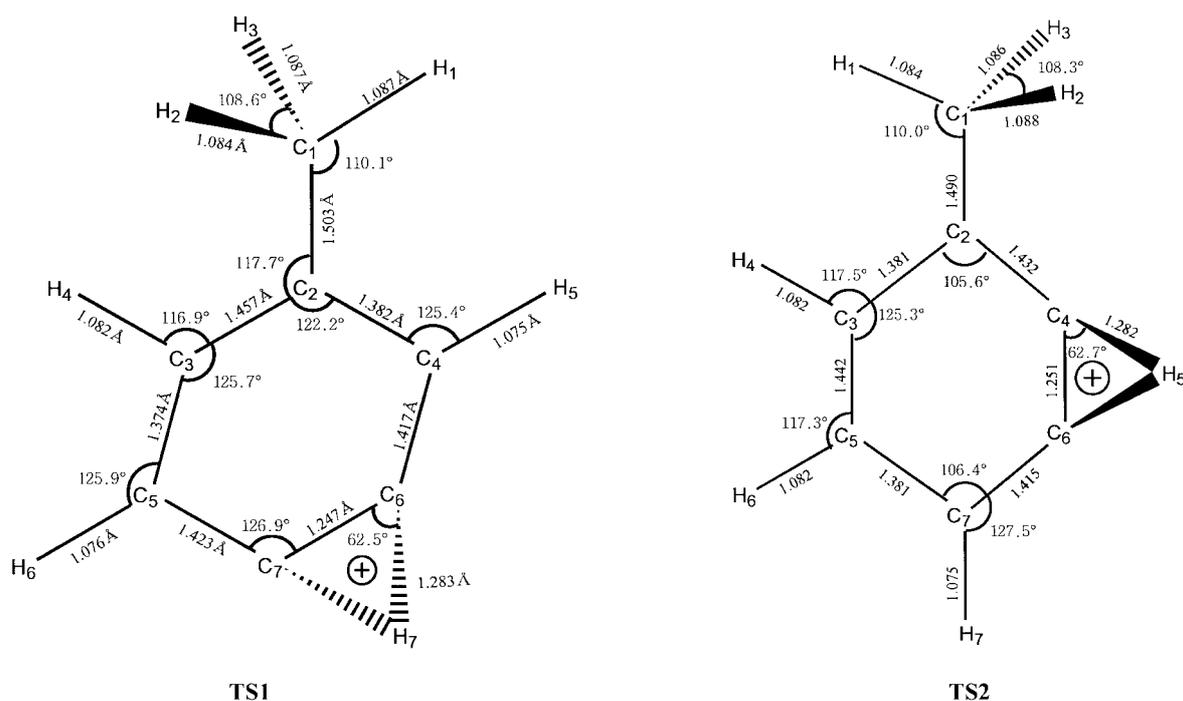

TS1   **TS2**

Figure 3. Predicted geometries for the transition states at the DZP CISD level of theory. **TS1** is the transition state for the arrangement between the *o*- and the *m*-tolyl cations, and **TS2** is the transition state for the arrangement between the *m*- and the *p*-tolyl cations. Bond lengths are in Å and bond angles are in degrees.

triple excitations included perturbatively, so called CCSD(T), do not change significantly the geometries of the tolyl cations. The C-C bond distances between the methyl moiety and the six-membered ring are predicted to be 1.512 Å for *o*-tolyl and 1.515 Å for *m*- and *p*-tolyl cations, which show pure single-bond character. The C-C bond distances directly connected to the positively charged carbon are shortened to be 1.34-1.35 Å, which show more π characters. The C-C-C bond angles between these carbons are predicted to be 149°, 148.0°, and 147.1° for the *o*-, *m*-, and *p*-tolyl cations respectively. The *Cs* symmetry planes for the *o*- and *m*-tolyl cations include the six-membered ring and one C-H bond in methyl group, while the plane for the *p*-tolyl cation is perpendicular to the ring. For the *m*-tolyl cation, the optimized geometries have *Cs* symmetry at the DZ and DZP SCF levels of theory, and the C_1 symmetry at the TZP SCF level

of theory. This means that the inclusion of more basis set is important for the precise prediction of the geometrical parameters of the *m*-tolyl cation.

The optimized geometries at the DZP CISD level of theory have been shown in Figure 3(a) for the transition state (**TS1**) between *o*- and *m*-tolyl cations and in Figure 3(b) for the transition state (**TS2**) between *m*- and *p*-tolyl cations. In these structures, the ring strain between three-membered and six-membered rings distorted the ring structures to have C_1 symmetry. And in three-membered rings, the C-C bond distances are shortened to be 1.247 and 1.251 Å for **TS1** and **TS2**, respectively, which show almost double bond character and the C-H bond distances are predicted to be 1.283 and 1.282 Å, respectively.

Vibrational frequencies. The harmonic vibrational frequencies and ZPVEs for the optimized geometries of the

Table 6. Harmonic vibrational frequencies (in cm^{-1}) and zero-point vibraional energies (ZPVE, in kJ/mol) for the isomers of $C_7H_7^+$ at the DZP and TZP SCF levels of theory

	DZP SCF					TZP SCF				
	Tropylium	Benzyl	*o*-tolyl	*m*-tolyl	*p*-tolyl	Tropylium	Benzyl	*o*-tolyl	*m*-tolyl	*p*-tolyl
ω_1	3395	3442	3420	3429	3424	3358	3405	3390	3401	3396
ω_2	3390	3412	3413	3412	3421	3352	3377	3377	3386	3392
ω_3	3390	3410	3397	3409	3387	3352	3354	3360	3373	3351
ω_4	3380	3391	3378	3389	3387	3340	3354	3342	3351	3350
ω_5	3380	3388	3337	3319	3312	3340	3352	3304	3285	3280
ω_6	3371	3385	3314	3292	3292	3330	3346	3278	3258	3257
ω_7	3371	3337	3227	3214	3213	3330	3303	3201	3188	3188
ω_8	1763	1760	1887	1879	1866	1761	1753	1891	1883	1872
ω_9	1763	1721	1636	1621	1669	1761	1716	1629	1617	1658
ω_{10}	1625	1716	1601	1617	1606	1634	1708	1605	1613	1609
ω_{11}	1625	1615	1599	1593	1605	1634	1616	1599	1601	1609
ω_{12}	1599	1581	1594	1580	1550	1591	1580	1597	1571	1552
ω_{13}	1599	1474	1536	1539	1498	1591	1476	1538	1541	1496
ω_{14}	1547	1460	1481	1496	1491	1556	1462	1480	1493	1488
ω_{15}	1366	1456	1388	1377	1396	1372	1442	1390	1376	1403
ω_{16}	1366	1287	1316	1254	1297	1372	1290	1314	1254	1286
ω_{17}	1331	1260	1243	1227	1224	1334	1263	1246	1224	1226
ω_{18}	1331	1242	1206	1168	1193	1334	1235	1209	1168	1191
ω_{19}	1159	1212	1156	1157	1163	1136	1213	1158	1156	1164
ω_{20}	1159	1133	1152	1144	1116	1136	1122	1151	1143	1117
ω_{21}	1142	1098	1084	1118	1083	1132	1089	1079	1119	1083
ω_{22}	1142	1097	1066	1070	1049	1132	1088	1066	1071	1045
ω_{23}	1075	1086	1028	1010	1042	1073	1085	1017	1000	1036
ω_{24}	1075	1070	1015	991	995	1073	1074	1015	989	998
ω_{25}	963	1055	948	960	987	965	1051	950	963	988
ω_{26}	963	924	852	856	837	965	924	846	856	839
ω_{27}	928	871	801	787	811	938	866	796	785	812
ω_{28}	928	867	721	682	636	938	863	723	676	628
ω_{29}	928	703	712	671	628	928	699	718	673	621
ω_{30}	720	683	609	594	576	721	651	605	590	580
ω_{31}	604	647	503	460	511	595	651	500	458	510
ω_{32}	604	566	451	447	452	595	571	450	444	453
ω_{33}	464	454	431	422	389	468	445	435	427	395
ω_{34}	464	382	298	366	360	468	384	301	370	362
ω_{35}	243	373	194	219	252	239	371	192	216	252
ω_{36}	243	185	31	11	13	239	179	24	26	27
ZPVE	331.4	327.4	317.2	315.6	315.3	329.5	325.4	315.7	314.3	314.1

tropyrium, benzyl, and three isomers of tolyl ions at the SCF level of theory with DZP and TZP basis sets are listed in Table 6. The real vibrational frequencies for five $C_7H_7^+$ cations confirm that they are all true minima. The total 36 vibrational modes include seven C-H stretching, seven C-C stretching, thirteen C-C-H or H-C-H bending, and nine torsional modes. The effect of increasing basis set from DZP to TZ2P decreases the vibrational frequencies by about 25-40 cm^{-1} for the C-H stretching modes, while it does not change too much (about ≤ 10 cm^{-1}) for other modes. The lowest torsional frequencies are calculated to be 239 and 179 cm^{-1} for tropyrium and benzyl ions, and to be 24, 26, and 27 cm^{-1} for *o*-, *m*-, and *p*-tolyl cations, respectively, at the TZP SCF level of theory. The zero-point vibrational energies have been used to calculate relative energies of $C_7H_7^+$ isomers.

Table 7. Harmonic vibrational frequencies (in cm^{-1}) and zero-point vibrational energies (ZPVE, in kJ/mol) for the transition states between tolyl cations at the SCF level of theory

	TS1			**TS2**		
	DZ SCF	DZP SCF	TZP SCF	DZ SCF	DZP SCF	TZP SCF
ω_1	3500	3455	3423	3495	3450	3418
ω_2	3426	3382	3346	3489	3447	3417
ω_3	3412	3371	3334	3414	3475	3338
ω_4	3342	3321	3287	3337	3319	3287
ω_5	3310	3290	3253	3307	3284	3249
ω_6	3227	3213	3188	3223	3209	3184
ω_7	2202	2318	2286	2200	2331	2296
ω_8	2047	2205	2203	2103	2209	2213
ω_9	1639	1681	1673	1654	1682	1674
ω_{10}	1630	1599	1601	1633	1609	1608
ω_{11}	1627	1596	1592	1631	1593	1596
ω_{12}	1588	1589	1586	1580	1548	1544
ω_{13}	1564	1546	1547	1525	1540	1532
ω_{14}	1498	1458	1459	1448	1482	1480
ω_{15}	1411	1402	1403	1440	1411	1415
ω_{16}	1356	1357	1352	1336	1287	1286
ω_{17}	1274	1253	1256	1270	1258	1256
ω_{18}	1199	1172	1173	1259	1239	1233
ω_{19}	1194	1158	1161	1195	1153	1155
ω_{20}	1118	1092	1090	1127	1102	1102
ω_{21}	1106	1088	1083	1108	1085	1085
ω_{22}	1033	1031	1031	1054	1040	1036
ω_{23}	1014	1008	1009	992	960	964
ω_{24}	962	914	920	979	942	944
ω_{25}	878	867	871	921	888	888
ω_{26}	841	828	828	802	808	809
ω_{27}	735	758	760	713	693	694
ω_{28}	613	582	580	636	614	610
ω_{29}	576	543	542	588	573	573
ω_{30}	547	513	518	485	529	523
ω_{31}	494	388	410	442	374	392
ω_{32}	345	348	349	377	364	372
ω_{33}	258	333	336	314	350	354
ω_{34}	136	201	204	240	228	228
ω_{35}	102	133	128	117	146	141
ω_{36}	1621*i*	1255*i*	1257*i*	1572*i*	1217*i*	1217*i*
ZPVE	306.3	305.0	303.8	307.6	305.8	304.4

The harmonic vibrational frequencies and ZPVEs for the transition states between tolyl cations have been listed in Table 7. A single imaginary vibrational frequency for each transition state confirms the true transition state. The imaginary vibrational frequencies of 1257*i* and 1217*i* cm^{-1} for **TS1** and **TS2**, respectively, can be assigned to the C-C-H bending mode due to the 1,2-hydrogen shift.

Relative energies. The absolute and relative energies of $C_7H_7^+$ isomers at various levels of theory are listed in Table 8. The absolute energies are calculated at the fully optimized geometries except at the DZP CCSD(T) level of theory, which is too big for full optimizations. Therefore, the DZP CCSD(T) energies are obtained by single-point energy calculations at the DZP CCSD optimized geometries. The relative energies (ΔE) are with respect to the tropylium cation, which has the lowest energy among $C_7H_7^+$ isomers, and include the ZPVE corrections based on the SCF vibrational frequencies with the corresponding basis set. And the ZPVEs have been scaled for energy corrections by the factor of 0.91.[34] In addition, to compare our results with other theoretical predictions and experimental measurements, the experimental heat of formation, $\Delta H_{f0}^{\circ} = 919$ kJ/mol for the benzyl cation is taken as a base level, as recommended by Shin.[23] In this way, the 0 K heats of formation for other $C_7H_7^+$ isomers are predicted to be 890, 1095, 1101, and 1110 kJ/mol for the tropylium, *o*-, *m*-, and *p*-tolyl cations, respectively, and compared with other theoretical and experimental results in Table 8. In general, the high level calculation like CCSD or CCSD(T) is recommended to be used with the large basis set such as triple zeta plus two sets of polarization functions (TZ2P) for the best prediction. However, the TZ2P basis set is too large for $C_7H_7^+$ system because of the limitation of the computer facility. In this study, we just used the TZP basis set for the SCF calculation to look at the basis set effect. The relative energies are increased going from DZP SCF to TZP SCF by 3.8 kJ/mol for the benzyl cation and 1.9-2.7 kJ/mol for the tolyl cations. Therefore, the energy differences between the benzyl and tolyl cations might be decreased by employing the large basis set at the CCSD or CCSD(T) level of theory.

Our best prediction for the relative energy of benzyl cation with respect to the tropyrium ion is 28.5 kJ/mol, which is in good agreement with the previous theoretical predictions of 29 kJ/mol by Nicolaides and Radom,[22] and of 23 kJ/mol by Shin,[23] while a recent DFT calculation shows a little high relative energy of 38 kJ/mol by Ignatyev and Sundius.[24] The experimental observations for the 0 K heats of formation are in the range of 870-890 kJ/mol for tropylium and 916-935 kJ/mol for benzyl cation.[23,24] The ΔH_{f0}° values of 1095, 1101, and 1110 kJ/mol for *o*-, *m*-, and *p*-tolyl are in very good agrement with the recent theoretical predictions of 1091, 1098, and 1107 kJ/mol by Ignatyev and Sundius[24] for both in magnitude and in order of relative stabilities. And they are about 8-9 kJ/mol higher in energy than the theoretical results estimated by Shin[23] but the order of relative stabilities and the relative energies between tolyl cations of 6 kJ/mol for *ortho-meta* and 8 kJ/mol for *meta-para* are still in good

Table 8. Absolute (in hartree) and relative energies (ΔE, in kJ/mol) of $C_7H_7^+$ isomers at various levels of theory

Level \ Isomers	Tropylium	ΔE	Benzyl	ΔE	*o*-tolyl	ΔE	*m*-tolyl	ΔE	*p*-tolyl	ΔE
DZ SCF	−268.818024	0	−268.806489	26.3	−268.720155	244.4	−268.715861	254.2	−268.713789	259.6
DZP SCF	−268.936008	0	−268.927981	17.5	−268.846653	221.7	−268.842266	231.7	−268.839649	238.3
TZP SCF	−268.969491	0	−268.959957	21.3	−268.879681	223.6	−268.875460	232.9	−268.872977	239.4
DZ CISD	−269.399628	0	−269.385139	34.0	−269.304560	237.0	−269.301489	243.7	−269.298827	250.6
DZP CISD	−269.770980	0	−269.760044	25.1	−269.683748	216.1	−269.680382	223.5	−269.677417	230.9
DZ CCSD	−269.434413	0	−269.419462	35.3	−269.344766	222.8	−269.341958	228.7	−269.339119	236.1
DZP CCSD	−269.869120	0	−269.857069	28.0	−269.785539	206.5	−269.782490	213.0	−269.779424	220.8
DZ CCSD(T)	−269.459447	0	−269.444987	34.0	−269.370480	221.0	−269.368008	226.1	−269.364789	234.4
DZP CCSD(T)[a]	−269.912086	0	−269.899863	28.5	−269.829161	204.8	−269.826432	210.5	−269.823032	219.1
This work	890		(919)		1095		1101		1110	
theory	898[b]		926[b]							
	896[c]		(919)[c]		1087[c]		1093[c]		1101[c]	
	881[d]		(919)[d]		1091[d]		1098[d]		1107[d]	
expt			919 ± 5[e]				1074[e], 1079[f]		1094[e], 1096[f]	
					1080[g]		1091[g]		1083[g]	
	870-890[h]		916-935[h]							

The relative energies with respect to the tropylium cation include zero-point vibrational energy (ZPVE) corrections. [a]The DZP CCSD(T) energy is a single-point energy at the DZP CCSD optimized geometry. [b]Reference 22. [c]Reference 23. [d]Reference 24. [e]Reference 14. [f]Reference 35. [g]Reference 1. [h]Reference 23 and reference 24 and more references cited therein.

agreement with our predictions of 6 and 9 kJ/mol, respectively. However, the experimental 0 K heats of formation for the tolyl cations are still in struggles. The experimental observations for the ΔH_{f0}° values are 1074, 1079, and 1091 kJ/mol for the *m*-tolyl cation and 1094, 1096, and 1083 kJ/mol for the *p*-tolyl cation. The only available experimental 0 K heat of formation for the *o*-toly cation is measured to be 1080 kJ/mol. The significant discrepancy between the experimental observation by Lin *et al.*[1] and theoretical predictions is the relative stability of the *o*-, *m*-, and *p*-tolyl cations.

The relative energies of the tolyl cations and the transition states with respect to the *o*-tolyl cation are shown in Table 9. The energy barrier for the rearrangement of the *o*-tolyl cation into *m*-tolyl isomer by 1,2-hydrogen shift is predicted to be 214 kJ/mol (51.2 kcal/mol) at the DZP CISD level of

Table 9. Relative energies (ΔE, in kJ/mol) of tolyl cations and the transition states (**TS1** and **TS2**) between them at various levels of theory

	o-tolyl	TS1	*m*-tolyl	TS2	*p*-tolyl
DZ SCF	0	281(67.2)	10	294(70.3)	15
DZP SCF	0	244(58.3)	10	252(60.2)	17
TZP SCF	0	240(57.4)	9	248(59.3)	16
DZ CISD	0	241(57.6)	7	250(59.8)	12
DZP CISD	0	210(51.2)	7	222(53.1)	15
DZ CCSD	0	–	6	–	13
DZP CCSD	0	–	7	–	14
DZ CCSD(T)	0	–	5	–	13
DZP CCSD(T)	0	–	6	–	15

The relative energies with respect to the *o*-tolyl cation include zero-point vibrational energy (ZPVE) corrections. Values in parentheses are in kcal/mol.

theory. The previous prediction of the barrier height for the 1,2-hydrogen shift from the *o*-tolyl cation to the *m*-tolyl cation had been reported to be 47.0 kcal/mol after the ZPVE correction from the DFT calculation by Ignatyev and Sundius.[24] And the energy barrier for the rearrangement of the *m*-tolyl cation to the *o*-tolyl cation was predicted to be 38.9 kcal/mol by the MINDO/3 calculation.[21] The barrier height for the 1,2-hydrogen shift from the *m*-toly cation to the *p*-tolyl cation is also predicted to be 222 kJ/mol (53.1 kcal/mol) at the DZP CISD level of theory, which is only slightly higher than the height for the interconversion of the *o*-tolyl to the *m*-tolyl cation. The barriers for the 1,2-hydrogen shift, predicted in this study, is relatively higher in energy than those of the previous theoretical (DFT or MINDO/3) predictions. The barrier heights for the rearrangements among the three tolyl isomers by 1,2-hydrogen shift are much higher than the barrier height for the rearrangement of the *o*-toly cation into the benzyl cation, which was predicted to be 24.8 kcal/mol by Ignatyev and Sundius.[24] Therefore, it is expected that the rearrangements of the *m*-tolyl and the *p*-tolyl cation to the *o*-tolyl cation by the 1,2-hydrogen shift is not an energy-efficient channels for them to rearrange to the benzyl cation. It calls for more theoretical study to establish the rearrangement mechanisms of the *m*-tolyl and the *p*-tolyl cation to the benzyl cation and the tropylium cation.

Conclusions

The equilibrium structures for the tropylium and benzyl cations which have relatively high symmetry (like C_{2v}) have been fully optimized at the DZP CCSD(T) levels of theory. However the structures of *o*-, *m*- and *p*-tolyl cations which have C_s or C_1 symmetries are optimized fully up to the DZP

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CCSD and DZ CCSD(T) levels of theory. The C-C bond distances directly connected to the positively charged carbon on tolyl cations are predicted to be 1.34-1.35 Å, which show relatively more π characters. The C-C-C bond angles between these carbons are predicted to be 149°, 148.0°, and 147.1° for the *o*-, *m*-, and *p*-tolyl cations respectively. The geometries for the transition states (**TS1** and **TS2**) between three structural isomers of tolyl cations which have C_1 symmetry have been optimized up to DZP CISD level of theory. Because of the ring strain between three- and six-membered rings, the three-membered ring structures in both TS1 and TS2 are distorted to have C_1 symmetry. The harmonic vibrational frequencies for tropylium, benzyl and three isomers of tolyl cations are all real numbers, which confirm the potential minima and each unique imaginary vibrational frequencies confirm the true transition states.

The relative energy of benzyl cation with respect to the tropyrium ion is predicted to be 28.5 kJ/mol and is in good agreement with the previous theoretical predictions. The 0 K heats of formation, ΔH°_{f0}, have been predicted to be 890, 1095, 1101, and 1110 kJ/mol for tropylium, *o*-, *m*-, and *p*-tolyl cations by taking the experimental value of 919 kJ/mol for the benzyl cation as the base level. The relative stabilities between three position isomers of tolyl cations are *ortho < meta < para*, which is in good agreement with previous theoretical predictions, but is in disagreement with the experimental observation by Lin *et al.*.[1] The predicted relative energies of 0, 6, 15 kJ/mol in the series *o*-, *m*-, *p*-tolyl are in excellent agreement with previous predictions by Ignatyev and Sundius,[25] and Shin.[24] The activation energy barriers are predicted to be 51.2 kcal/mol for the rearrangement of the *o*-tolyl into the *m*-tolyl cation and 53.1 kcal/mol for the conversion of the *m*-toly cation into the *p*-tolyl cation.

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