

# Theoretical study of the potential energy surface for CH<sub>3</sub> and CH<sub>4</sub> losses from ethyltoluenes

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Received: 19 June 2009 / Accepted: 9 September 2009 / Published online: 23 September 2009  
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**Abstract** The decomposition of *o*-, *m*-, and *p*-ethyltoluene has been studied by density functional theory. It was found that monomolecular homolytic methyl loss from ethyl moiety seems to be the most favorable mechanism than other proceeding through ethyl, ring-methyl and hydrogen loss. Two possible channels of methane elimination from *o*-ethyltoluene were studied at B3LYP/6-311++G(df,p) level of theory.

**Keywords** B3LYP · Ethyltoluene · Decomposition · Tolylycarbene

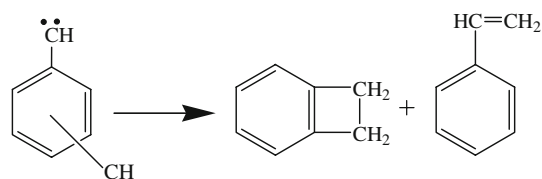
## 1 Introduction

The mechanism of simple aromatic derivatives has been a problem of longstanding interest in organic chemistry. The decomposition of aromatic compounds has been the subject of more experimental and theoretical research. Study of the mechanism of high-temperature thermal decomposition of simple aromatic derivatives is of great interest, because of their industrial importance [1, 2]. The effect of substituents on the properties of aromatic compounds has traditionally played an important role in organic chemistry. There are two possible channels for the decomposition of *o*-, *m*-, and *p*-ethyltoluene as described in following. The first mechanism is the dissociation through the direct breaking for  $\beta$  C–C bond. The second possible mechanism involves methane elimination. In 1980, Barton and Steln [3] published a very low pressure pyrolysis study of alkyl

benzenes. They concluded that activation energy differences had been approximately separable into *ortho* and non-*ortho* contributions, amounting to a lowering of the activation energy, relative to ethylbenzene, of 1.3–1.7 kJ/mol per *m*- or *p*-CH<sub>3</sub>, and 5.0–6.3 kJ/mol per *o*-CH<sub>3</sub>. The gamma radiolysis of ethyltoluene was investigated in the liquid state by Weis and Rao [4]. *p*-Ethyltoluene deuterated in the methyl group was irradiated in attempt to determine the origin of the methane and the C<sub>2</sub> hydrocarbons. They also reported that at least 90% of the gases produced originate from the ethyl group of the molecule.

To our knowledge, there is no theoretical study on decomposition of ethyltoluenes. Therefore, we decided to make an extensive study of their potential energy surfaces (PES), using quantum chemistry methods, with the purpose of determining whether or not the activation energies for methane elimination are higher than for the methyl loss reactions.

Our computational exploration reveals that methane elimination from ethyltoluenes is mediated by tolylycarbenes. In 1971, Hedaya [5] reported the thermal rearrangement of *o*-, *m*-, and *p*-tolylcarbenes to benzocyclobutene and styrene:



Latter Chapman et al. [6] reported a matrix-isolation study on the rearrangement of tolylycarbenes. They proposed a simpler  $\sigma$ -based mechanism involving a series of ring-expansions and contractions of tolylycarbenes and methylcycloheptatetraenes. However, they did not observe

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bicyclo[4.1.0]hepta-2,4,6-triene (BCT) as an intermediate. The effect of aryl substituents on the interconversion of BCT has been studied by Geise and Hadad [7] at B3LYP/6-311+G(d,p). Warmuth et al. [8] had successfully measured the activation energies for the enantiomerization of the highly strained 5-methylcycloheptatetraene and its rearrangement to *m*-, and *p*-tolylcarbenes. These values had provided the first experimental support for the results of recent ab initio calculations [7].

In accordance with the Chapman mechanism the *m*-, and *p*-tolylcarbenes rearrangement is mediated by *o*-tolylcarbene [8]. Therefore, we investigated the rearrangement of *o*-tolylcarbene.

## 2 Computational details

Ab initio and DFT calculations were carried out using the GAUSSIAN 98 program [9] package. B3LYP method, which includes Becke's exchange potential [10] and the Lee–Yang–Parr correlation potential [11] was chosen to perform calculations at the DFT level. Structure optimizations were performed with a Pople's 6-311++G(df,p) basis set [12]. The ab initio calculations were realized at MP2 level of theory [13] with 6-31G(d) basis set. The nature of the stationary points was then checked by counting no imaginary frequency for stable species and a single for transition states. Transition states have been verified by calculating intrinsic reaction coordinates (IRC).

## 3 Results and discussion

### 3.1 Decomposition via homolytic bond fission

Our first approach to the problem was to estimate the activation energies of methyl loss from ethyltoluenes. The activation energies  $E_a$  were computed using Eq. 1:

$$E_a = D(R_1-R_2) + RT, \quad (1)$$

where  $D(R_1-R_2)$  is the dissociation energy of the  $R_1-R_2$  bond,  $R_1$  and  $R_2$  are radicals left after the bond

decomposition,  $T$  is the temperature in which the experimental was carried out.  $D(R_1-R_2)$  can be calculated according to Eq. 2:

$$D(R_1 - R_2) = \Delta H_f^\circ(R_1) + \Delta H_f^\circ(R_2) - \Delta H_f^\circ(R_1 - R_2) \quad (2)$$

where  $\Delta H_f^\circ(R_1)$  and  $\Delta H_f^\circ(R_2)$  are the enthalpies of the formation of radicals,  $\Delta H_f^\circ(R_1-R_2)$  is the enthalpy of formation of the initial compounds. The temperature at which the ethyltoluenes pyrolysis was studied is in the range of 1,050–1,200 K [3]. The activation energies calculated for 1,200 K at various levels of theory are collected in Table 1.

HF level of theory with 6-31G(d) basis set gives the lowest estimations of activation energies, whereas at the MP2/6-31G(d) level of theory the activation energies are predicted to be much higher than experimental value. The B3LYP/6-311++G(df,p)—calculated activation energies are in good agreement with experimental data. The deviation from available experimental data is less 0.3 kcal/mol. Therefore, we conclude that the B3LYP/6-311++G(df,p) level of theory do provide a reasonable way to tackle the problem of the decomposition channels of ethyltoluenes.

The competitive simple bond rupture mechanisms, proceeding through homolytic C–C and C–H bonds fission, without an apparent transition state structure, were studied at B3LYP/6-311++G(df,p) level of theory (Table 2).

Tables 1 and 2 show that methyl loss from ethyl moiety seems to be the most favorable mechanism than other proceeding through ethyl, ring-methyl and hydrogen loss.

### 3.2 Methane elimination

Table 3 presents the results of methane elimination from *o*-, *m*-, *p*-ethyltoluenes. Methane elimination from ethyltoluenes is preceded by a mechanism requiring an elongation of the C–C and C–H bonds of ethyl moiety.

Structure and selected geometrical parameters of transition state (TS1) for methane elimination from *o*-ethyltoluene is depicted in Fig. 1. At the transition state structure TS1, the C3–C8 and C8–H18 bonds lengths are 1.445 and 1.384 Å, respectively. An IRC calculations starting at TS1 leading to a singlet state of *anti-ortho*-methylphenylcarbene (4a, Fig. 2) and methane. The potential energy profile for reactions of

**Table 1** Calculated and experimental values of the activation energy ( $E$ ) of the methyl loss from ethyltoluenes (1,200 K)

Reaction	$E_a$ (kcal/mol)				Experiment [3]
	Method				
	HF/ 6-31G(d)	MP2/ 6-31G(d)	B3LYP/ 6-31G(d)	B3LYP/ 6-311++G(df,p)	
1-CH <sub>3</sub> ,2-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> →1-CH <sub>3</sub> ,2-CH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> + CH <sub>3</sub> ·	41.6	106.4	74.8	70.5	70.7
1-CH <sub>3</sub> ,3-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> →1-CH <sub>3</sub> ,3-CH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> + CH <sub>3</sub> ·	42.4	106.8	75.7	71.8	71.5
1-CH <sub>3</sub> ,4-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> →1-CH <sub>3</sub> ,4-CH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> + CH <sub>3</sub> ·	39.9	106.7	75.5	71.2	71.5

**Table 2** Calculated dissociation energies [D(R<sub>1</sub>–R<sub>2</sub>)]of the C–C and C–H bonds in ethyltoluenes [B3LYP/6-311++G(df,p)]

Reaction	D(R <sub>1</sub> –R <sub>2</sub> ), kcal/mol
1-CH <sub>3</sub> ,2-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> →1-CH <sub>3</sub> ,2-CH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> + CH <sub>3</sub> ·	68.1
1-CH <sub>3</sub> ,3-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> →1-CH <sub>3</sub> ,3-CH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> + CH <sub>3</sub> ·	69.4
1-CH <sub>3</sub> ,4-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> →1-CH <sub>3</sub> ,4-CH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> + CH <sub>3</sub> ·	68.8
1-CH <sub>3</sub> ,2-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> → <i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> · + C <sub>2</sub> H <sub>5</sub> ·	90.5
1-CH <sub>3</sub> ,3-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> → <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> · + C <sub>2</sub> H <sub>5</sub> ·	92.1
1-CH <sub>3</sub> ,4-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> → <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> · + C <sub>2</sub> H <sub>5</sub> ·	92.6
1-CH <sub>3</sub> ,2-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> → <i>o</i> -C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> · + CH <sub>3</sub> ·	93.9
1-CH <sub>3</sub> ,3-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> → <i>m</i> -C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> · + CH <sub>3</sub> ·	95.6
1-CH <sub>3</sub> ,4-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> → <i>p</i> -C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> · + CH <sub>3</sub> ·	96.1
1-CH <sub>3</sub> ,2-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> → <i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> · + H·	98.1
1-CH <sub>3</sub> ,3-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> → <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> · + H·	99.3
1-CH <sub>3</sub> ,4-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> → <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> · + H·	99.2
1-CH <sub>3</sub> ,2-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> → <i>o</i> -C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> · + H·	86.2
1-CH <sub>3</sub> ,3-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> → <i>m</i> -C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> · + H·	86.3
1-CH <sub>3</sub> ,4-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> → <i>p</i> -C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> · + H·	86.0

**Table 3** Calculated activation enthalpies for methane loss from *o*-, *m*-, *p*-ethyltoluene at the B3LYP/6-311++G(df,p) level of theory

Reaction	ΔH <sub>298</sub> <sup>‡</sup> (TS1), kcal/mol
1-CH <sub>3</sub> ,2-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> → <i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> · + CH <sub>4</sub>	83.8
1-CH <sub>3</sub> ,3-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> → <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> · + CH <sub>4</sub>	84.5
1-CH <sub>3</sub> ,4-C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> → <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> · + CH <sub>4</sub>	85.0

methyl and methane loss from *o*-ethyltoluene is displayed in Fig. 2.

At the B3LYP/6-311++G(df,p) level, TS1 lies 83.8 kcal/mol above the *o*-ethyltoluene. The alternative reaction of *o*-xylylene (5, Fig. 2) formation from 1 has a

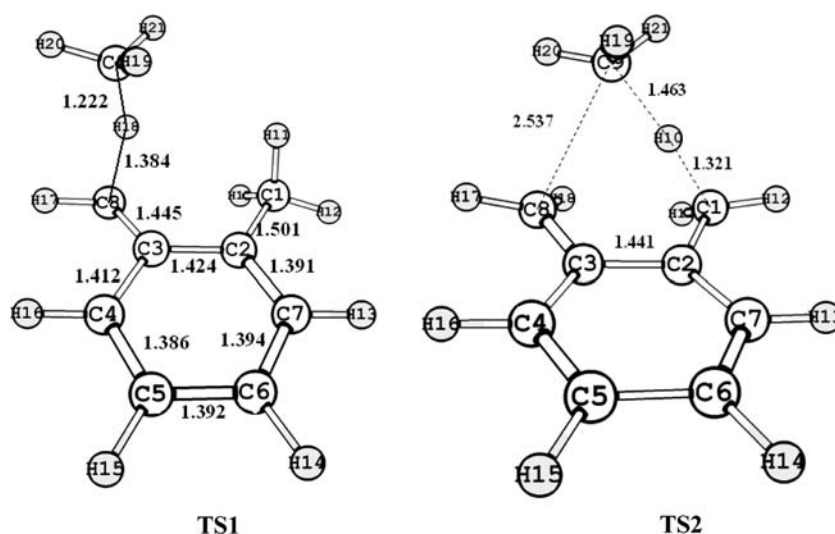
slightly lower activation barrier. The optimized structure TS2 (see Fig. 1) was characterized as a true transition state for this reaction. However, the formation of *o*-xylylene is possible for reaction of methane elimination only from *o*-ethyltoluene.

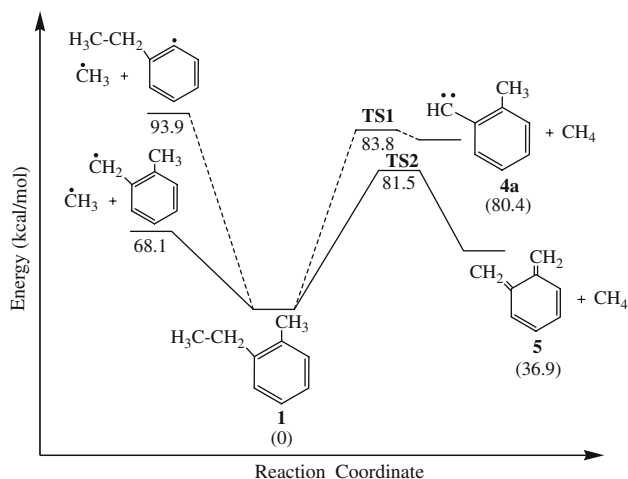
Experimental determination of thermodynamics parameters of 4 and 5 is limited by their high reactivity [6, 7, 14]. Gas-phase calculations for *o*-, *m*-, *p*-substituted phenylcarbenes demonstrate that aromatic ring substituents can have a large effect on the singlet–triplet splitting in these molecules [14]. Structure 4 is calculated to have a triplet ground state 5.8 kcal/mol (B3LYP/6-311++G(df,p)) more stable than singlet state. McMahon and Chapman [15] have shown that triplet carbene 4a decays thermally to singlet *o*-xylylene (5) in an argon matrix.

The conformation transition from 4a to *syn-ortho*-methylphenylcarbene (4b) was explored. The potential energy barrier corresponding to this conformation transition is calculated to be 11.3 kcal/mol. *Anti-syn* conformation transition is realized by rotation of CH-group about C–C bond and bridged by TS5 (see Fig. 4). The dihedral angle C2C3C8H16 is –92.7°, hence the hydrogen atom is placed above the ring plane. Structure 4b is calculated to lie only 1.1 kcal/mol above 4a.

Formation of 5 from 4a involved the intramolecular migration of the hydrogen atom (Fig. 3). The optimized geometrical parameters of transition state TS3 are depicted in Fig. 4. This transition state has C1H9 and C8H9 bond distances of 1.307 and 1.522 Å, respectively. The activation barrier is calculated to be 10.1 kcal/mol that is only 1.2 kcal/mol lower than activation barrier for conformation transition 4a→4b. Optimized structure 5 is calculated to be 42.6 kcal/mol lower than 4a.

The thermal conversion of 5 to benzocyclobutene (6) is the classic example of an electrocyclic reaction. Guner [16]

**Fig. 1** Optimized structures of the transition states TS1 and TS2 for reactions of methane elimination from *o*-ethyltoluene at the B3LYP/6-311++G(df,p) level (bond lengths in Å)



**Fig. 2** Schematic potential energy diagram showing the unimolecular reactions associated to IRC path on the *o*-ethyltoluene ground state PES

have assessed of the performance of OLYP and O3LYP, B3LYP with a three basis sets, 6-31G(d), 6-311+G(2d,p) and 6-311G(2df,2pd) in predicting activation enthalpies and reaction enthalpies for the test set of 11 pericyclic reactions, including for reaction ring closing of *o*-xylylene to benzocyclobutane. It is shown that B3LYP with a small basis set provides the best activation barrier for this reaction, so this provides a practical method for the exploration of hydrocarbon pericyclic reactions. Our calculations of activation enthalpy (0 K) at B3LYP/6-311++G(df,p) 27.4 kcal/mol are in good agreement with Guner's [16] calculated, 27.3 kcal/mol (B3LYP/6-31G(d)), and experimental, 29.2 kcal/mol, values [17].

It is shown that benzocyclobutenes behave in way that is more similar as cyclobutenes in manifesting the same torquoselectivity pattern [18]. However, the temperature chosen for thermolysis is crucial. Although reactions proceed more slowly at 120–140 °C, greater discrimination between the conrotatory modes is exercised.

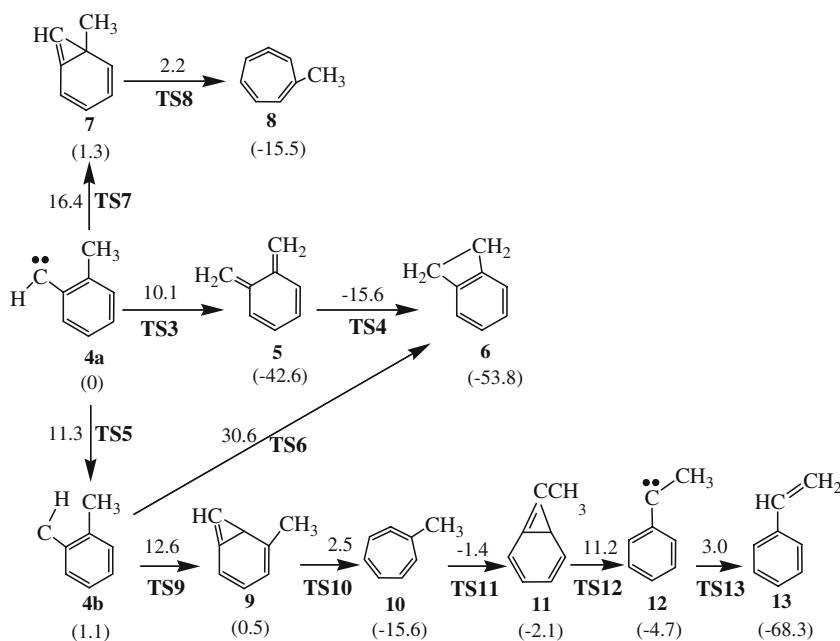
The next pathway we studied is formation of 6 from 4b. The energy of the transition state structure TS6 (Fig. 4) is very high, 29.5 kcal/mol, making this mechanism the most unlikely of the other possible channels. The intramolecular hydrogen shift takes place in this reaction, similar to that was observed for reaction 4a→5. The optimized transition state TS6 (Fig. 4) has C1H9 and C8H9 bond distances of 1.262 and 1.310 Å, respectively.

It is known that there is possible channel of the rearrangement of 4a and 4b proceeding through formation of methyl-substituted cycloheptatetraenes (8 and 10, Fig. 3). Earlier Chapman provided compelling spectroscopic and mechanistic evidence for 8 intermediates in the ring expansion of tolylcarbenes using matrix-isolation technique [6]. The rearrangement 4a to *anti-ortho* 7, via TS7 (Fig. 4), is endothermic by 1.3 kcal/mol, whereas for 4b to 9 exothermic by 0.6 kcal/mol.

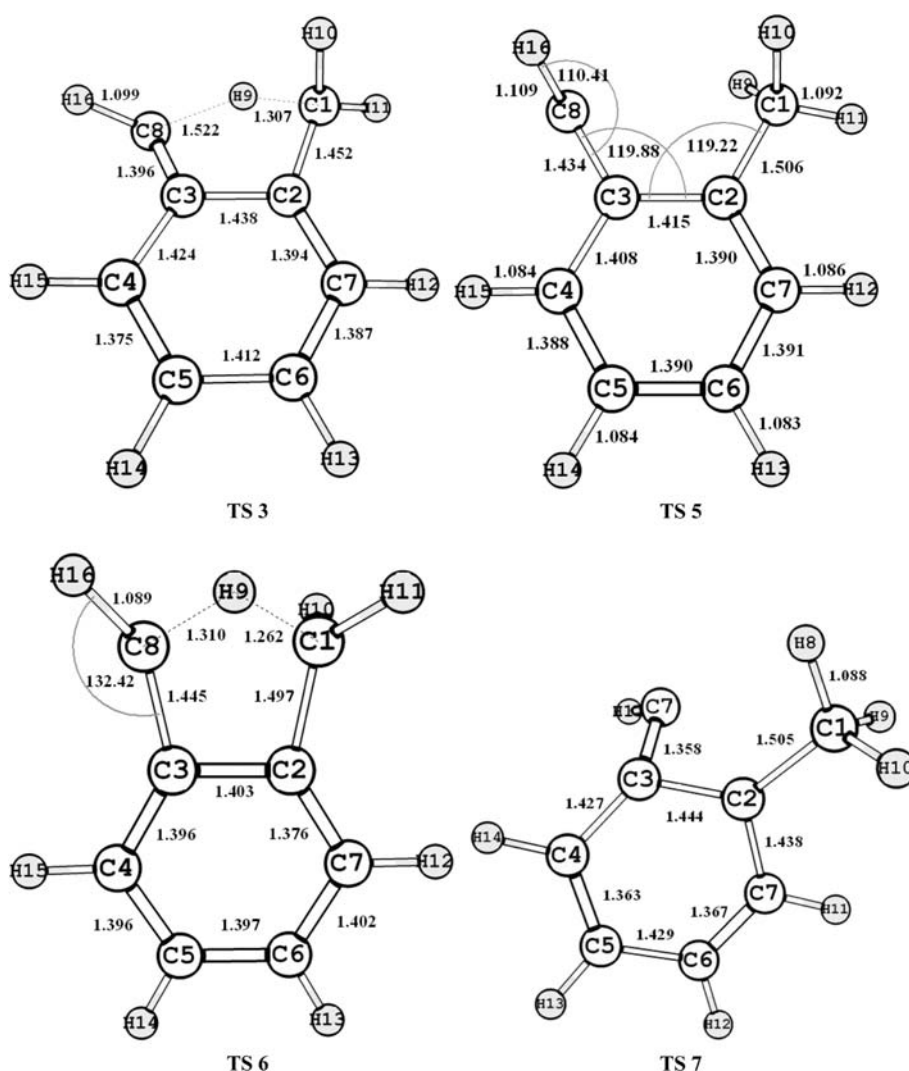
Formation of styrene (13, Fig. 3) from methylcycloheptatetraene (10) is mediated by 11 and 12 (Fig. 3). This mechanism was detected in the deuterium-labeling study of Trahanovsky and Scribner [19].

Therefore, the analysis of our calculated estimations and reliable data reported in the literature show that rearrangement of 4a to 5 seems to be the most favorable mechanism among the rest depicted in Fig. 3.

**Fig. 3** Rearrangement pathways of the *anti-ortho*-methylphenylcarbene (4a) obtained from the B3LYP/6-311++G(df,p) calculations. The energy of 4a is denoted as zero



**Fig. 4** Optimized structures of the transition states TS3, TS5, TS6, TS7 (bond lengths in Å and angles in degrees)



## 4 Conclusions

We have performed study of the decomposition channels on the potential energy surface of *o*-, *m*-, and *p*-ethyltoluene. Methyl loss from ethyl moiety seems to be the most favorable mechanism than other proceeding through ethyl, ring-methyl and hydrogen loss. The activation energy estimations for methane elimination from *o*-, *m*-, and *p*-ethyltoluene are calculated to be 83.8, 84.5, 85.0 kcal/mol, respectively. The alternative mechanism involved methane elimination from *o*-ethyltoluene with the *o*-xylylene formation is predicted to take place via transition structure lying 81.5 kcal/mol above the *o*-ethyltoluene. The rearrangement pathways of *anti-ortho*-methylphenylcarbene were studied.

The analysis of the results afforded from our exploration that the B3LYP/6-311++G(df,p) level of theory do provide a reasonable way to tackle the problem of the decomposition channels of ethyltoluenes (see Table 1).

**Acknowledgment** Our calculations were realized using the Interdepartmental Supercomputer Center (Moscow).

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