



## DFT, FT-Raman and FT-IR investigations of 5-o-tolyl-2-pentene

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## ABSTRACT

FT-IR and Raman spectra of 5-o-tolyl-2-pentene (OTP) have been experimentally reported in the region of 4000–10 cm<sup>-1</sup> and 4000–100 cm<sup>-1</sup>, respectively. The optimized geometric parameters, normal mode frequencies and corresponding vibrational assignments of cis and trans isomers of OTP (C<sub>12</sub>H<sub>16</sub>) have been theoretically examined by means of B3LYP hybrid density functional theory (DFT) method together with 6-31G(d) and 6-31++G(d,p) basis sets. Furthermore, reliable vibrational assignments have made on the basis of potential energy distribution (PED) calculated. Comparison between the experimental and theoretical results indicates that density functional B3LYP method is able to provide satisfactory results for predicting vibrational wavenumbers and trans isomer is supposed to be the most stable form of OTP molecule.

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## 1. Introduction

OTP has been part of many different scientific studies. For example, there are spectroscopic studies and cycloisomerization of OTP absorbed on many different zeolites which are applied in drying of process air, CO<sub>2</sub> removal from natural gas, CO removal from reforming gas, air separation, catalytic cracking, and catalytic synthesis and reforming [1–4].

Density functional theory (DFT) has big popularity as a cost effective general procedure for studying the physical properties of molecules. Unlike Hartree Fock theory, DFT recovers electron correlation in the self-consistent Kohn–Sham procedure through the functions of electron density, so it is a cost effective and reliable method [5–9]. The DFT/B3LYP model exhibits good performance on electron affinities, excellent performance on bond energies and reasonably good performance on vibrational frequencies and geometries of organic compounds [5–15].

Even though, OTP has wide applications in zeolite science, there is no detailed information present in literature about its molecular structure and spectroscopic properties. A detailed quantum chemical study will aid in making definitive assignments to the fundamental normal modes of OTP and in clarifying the obtained experimental data for this molecule. Furthermore, the presented data as theoretically and experimentally may be helpful in context of the further studies of OTP in example for some catalyst purposes. The commercial product as OTP is sold as a mixture of cis and trans

isomers; therefore, the aim of the study is also to investigate the most stable isomer of OTP. In this work, FT-IR and FT-Raman spectra with the vibrational assignments of OTP have been reported. The vibrational frequencies and structural parameters of OTP are also calculated with PED data for the most stable isomer at B3LYP level of theory using the 6-31G(d) and 6-31++G(d,p) basis sets. The results of the theoretical and spectroscopic studies are reported here.

## 2. Experimental

A commercial sample of OTP was purchased (Aldrich, 98%) and used without further purification. FT-MIR spectrum of OTP was recorded in the region of 4000–400 cm<sup>-1</sup> with Perkin–Elmer FT-IR 2000 spectrometer at a resolution of 4 cm<sup>-1</sup>. FT-FIR spectrum was recorded with Bruker Optics IFS66 v/s FTIR spectrometer with the resolution of 2 cm<sup>-1</sup> in the spectral region of 400–10 cm<sup>-1</sup>. The Raman spectrum was obtained using a Bruker Senterra Dispersive Raman microscope spectrometer with 532 nm excitation from a 3B diode laser having 3 cm<sup>-1</sup> resolution in the spectral region of 4000–100 cm<sup>-1</sup>.

## 3. Calculations

Many possible conformers could be proposed for OTP (Fig. 1), but here the discussion was confined for trans and cis isomers of the title molecule. They are considered as cis and trans positions according to the same and opposing directions of the substituent groups in surrounding double bond between C9 and C10 atoms of OTP (Fig. 1). For the calculations, two forms of OTP were first

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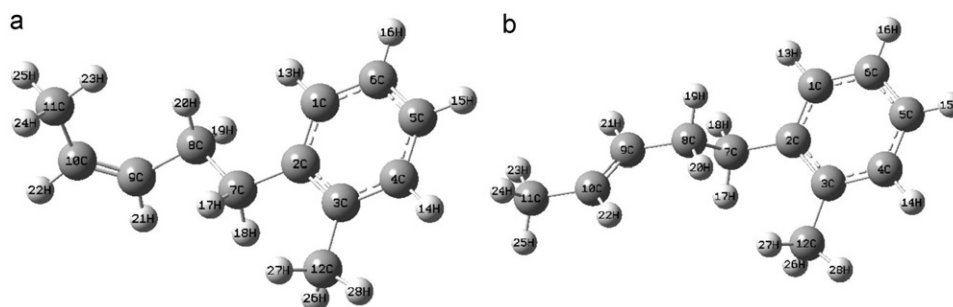


Fig. 1. Trans and cis isomers and numbering of OTP.

Table 1  
Some optimized features of two different isomers for OTP.

Medium	Isomerism			
	6-31G(d)		6-31++G(d,p)	
	Trans	Cis	Trans	Cis
Gas phase				
$G$ (Hartree)	−466.699261	−466.695407	−466.740360	−466.736666
Relative stability (( $G$ );kcal/mol)	0.00	2.42	0.00	2.32
Equilibrium constant ( $K_c$ )	0.0168		0.0199	
Mole percent (%)	98.35	1.65	98.05	1.95

optimized by B3LYP with 6-31G(d) and 6-31++G(d,p) basis sets in the gas phase. Trans isomer was found more stable than the cis form (Table 1). Therefore, for the vibrational calculations, the vibrational frequencies of trans form of OTP were calculated by using the same method and the basis sets under the keyword freq=Raman, and then scaled by 0.955 (above 1800  $\text{cm}^{-1}$ ) and 0.967 (under 1800  $\text{cm}^{-1}$ ) for 6-31G(d) and 0.955 (above 1800  $\text{cm}^{-1}$ ) and 0.977 (under 1800  $\text{cm}^{-1}$ ) for 6-31++G(d,p) [12,13,16]. No imaginary frequencies were observed; therefore, the optimized structure is a local minimum. All the calculations were performed by using Gaussian 03.C02 program [17] on a personal computer and GaussView 5.0.8 [18] and GaussSum 2.2.5 [19] programs were used for visualization of the structure and simulated vibrational spectra.

PED calculations; which show the relative contributions of the redundant internal coordinates to each normal vibrational mode of the molecule and thus make it possible to describe the character of each mode numerically; were carried out by the GAR2PED program [20] using the output files (as arch and log) created at the end of the frequencies calculations.

The mole fractions of individual conformers can be calculated with the following equations:

$$a \xrightleftharpoons{K_c} b$$

According to equilibrium given above,

$$K_c = \frac{N_a}{N_b} \quad \text{and} \quad N_a + N_b = 1$$

can be written, where  $K_c$  is conformational equilibrium constant between a and b forms,  $N_a$  and  $N_b$  are mole fractions of conformers a and b.  $N_a = 1/1 + K_c$ ,  $N_b = K_c/1 + K_c$ ,  $K_c = e^{-\delta\Delta G/RT}$ ,  $R = 1.987 \times 10^{-3}$  kcal/(mol K),  $T = 298$  K and  $\delta\Delta G = \Delta G_b - \Delta G_a$  [21].

## 4. Results and discussion

### 4.1. Geometrical structures

To study the vibrational frequencies, it is essential to examine the geometry of any compound as small changes in geometry can potentially cause substantial changes in frequencies. Gibbs free

energies, relative stability, equilibrium constant and mole percent of the optimized geometries in the gas phase of two conformations of OTP with B3LYP/6-31G(d) and B3LYP/6-31++G(d,p) are given in Table 1. Regarding the calculated free energies for gas phase, trans isomer is more stable than cis by 2.42 kcal/mol and 2.32 kcal/mol. Hence, OTP in the gas phase prefers trans form with the preference of 98.35% or 98.05%. Since mole percents of trans isomer in both basis sets are larger than cis isomer's values, the frequencies and assignments were determined considering trans form.

Table 2  
Some optimized geometrical parameters of OTP.

Geometrical parameters	B3LYP/6-31G(d)		B3LYP/6-31++G(d,p)	
	Trans	Cis	Trans	Cis
R(C–C) <sub>av</sub> /aromatic	1.399	1.400	1.401	1.401
R(C–H) <sub>av</sub> /aromatic	1.088	1.087	1.087	1.086
R(7,8)	1.551	1.540	1.551	1.540
R(8,9)	1.504	1.506	1.505	1.507
R(9,10)	1.336	1.339	1.338	1.341
R(10,11)	1.502	1.504	1.503	1.504
R(9–21)	1.093	1.092	1.093	1.091
R(10,22)	1.092	1.091	1.092	1.090
R(11–H) <sub>av</sub>	1.098	1.097	1.097	1.096
R(12–H) <sub>av</sub>	1.096	1.097	1.095	1.096
R(7–H) <sub>av</sub>	1.097	1.100	1.096	1.099
R(8–H) <sub>av</sub>	1.099	1.098	1.098	1.097
R(2,7)	1.516	1.520	1.516	1.520
R(3,12)	1.513	1.511	1.514	1.511
A(7,8,9)	112.69	111.71	112.77	111.75
A(8,9,10)	125.37	128.10	125.41	128.09
A(9,10,11)	125.34	128.13	125.39	128.09
A(1,2,7)	119.16	122.04	119.16	122.04
A(7,2,3)	121.90	119.31	121.92	119.34
A(2,7,8)	113.07	116.68	113.23	116.80
D(8,9,10,11)	179.71	0.53	179.93	0.25
D(1,2,7,8)	−89.39	0.80	−89.39	0.95
D(3,2,7,8)	89.05	−179.40	89.19	−179.27
D(7,2,1,6)	178.26	179.80	178.30	179.76
D(7,2,3,4)	−178.38	−179.80	−178.41	−179.76
D(7,2,3,12)	2.33	0.22	2.40	0.24
D(2,7,8,9)	178.16	177.58	177.75	177.35
D(7,8,9,10)	118.75	118.93	119.97	120.36

Av: average. Bond lengths, angle and dihedral angles are given as (Å) and ( $^\circ$ ), respectively.

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