

NMR, FT-IR, FT-Raman, UV spectroscopic, HOMO–LUMO and NBO analysis of cumene by quantum computational methods



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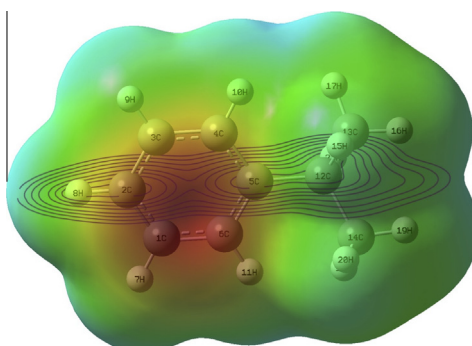
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HIGHLIGHTS

- The compound isopropyl benzene (cumene) has been investigated using FT-IR, FT-Raman and NMR and UV–Vis spectroscopic tool.
- The chemical shift of the compounds is found and it is favour for its change of chemical property.
- The stable geometry of the molecule through conformational study is carried out.
- The charge transfer in the molecule by HOMO–LUMO studied in relation with NBO analysis.

GRAPHICAL ABSTRACT

The isopropyl benzene (cumene) is an aromatic organic compound and is extensively studied due to its wide applications in biomedical and industrial fields. Considering its industrial and biomedical importance, a thorough analysis of physical and chemical properties is made for this molecule. It will be a helpful source to enrich the knowledge in the field of biomedical industries.



ARTICLE INFO

Article history:

Received 31 May 2014

Received in revised form 15 November 2014

Accepted 15 November 2014

Available online 21 November 2014

Keywords:

Cumene

Chemical shifts

Phenol

HOMO–LUMO

ABSTRACT

This work presents the investigation of cumene using the FT-IR, FT-Raman, NMR and UV spectra obtained through various spectroscopic techniques. The theoretical vibrational frequencies and optimized geometric parameters have been calculated by using HF and density functional theory with the hybrid methods B3LYP, B3PW91 and 6-311+G(d,p)/6-311++G(d,p) basis sets. The theoretical vibrational frequencies have been scaled and compared with the corresponding experimental data. ¹H and ¹³C NMR spectra were recorded and chemical shifts of the molecule were compared to TMS by using the Gauge-Independent Atomic Orbital (GIAO) method. A study on the electronic and optical properties, absorption wavelengths, excitation energy, dipole moment and frontier molecular orbital energies, and potential energy surface (PES) is performed using HF and DFT methods. The thermodynamic properties (heat capacity, entropy and enthalpy) at different temperatures are also calculated. NBO analysis is carried out to picture the charge transfer between the localized bonds and lone pairs. NLO properties related to polarizability and hyperpolarizability are also discussed.

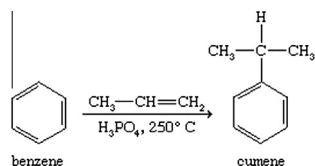
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Introduction

The other name of cumene is isopropyl benzene (ISPB) which consists aromatic hydrocarbon with aliphatic substitution. Benzene is converted to isopropyl benzene (cumene) by treatment with propylene and acidic catalyst.



Based on the simple aromatic structure it is generally assumed that under aerobic conditions isopropyl benzene is bio-degraded. But presence of the isopropyl moiety with the phenyl ring hinders microbial oxidation which results in lower degradation. Cumene undergoes oxidation to give cumene hydro peroxide. By the catalytic action of dilute sulphuric acid, cumene hydro peroxide is split into phenol and acetone [1]. Phenol in its various formaldehyde resins to bond construction materials like plywood and composition board (40% of the phenol produced) for the bisphenol A. It is also employed in making epoxy resins and polycarbonate (30%) and for caprolactam and also as starting material for nylon (20%). Cumene is also used in minor amount as a thinner for paints, enamels and lacquers [2].

A vibrational study and structural study have been carried out by Fishman et al. [9] in *ab initio* and normal coordinate analysis. Spectra of cumene and other alkyl benzenes, obtained with the help of the Time of Flight Mass Spectroscopy (TOFMS) technique were investigated in [3]. Lagowski et al. and Schaefer et al. [4,5] have made study on the theoretical simulations of molecule on the conformation study for the molecule and obtained two conformers at minimum energies 14.5 kJ/mol and 13.4 kJ/mol. In the present study a complete theoretical and spectroscopic investigation of ISPB are carried out which were not performed in the previous works.

Experimental details

The FTIR, FT Raman and FT NMR compound under investigation namely were obtained from M/S Aldrich Chemicals, USA. According to the report, the FT-IR spectrum of the compound was recorded in Perkin-Elmer 180 spectrometer between 4000 and 400 cm^{-1} with the spectral resolution is $\pm 2 \text{ cm}^{-1}$. The FT-Raman spectrum of the compound was recorded in the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.064 μm line widths with 200 mW powers. The frequencies of all sharp bands are accurate to $\pm 1 \text{ cm}^{-1}$. The high resolution H NMR and C NMR spectra were recorded using 300 MHz and 75 MHz NMR spectrometer respectively. The UV-Vis spectra were recorded in liquid phase dissolved in ethanol in the range of 200–400 nm, with the scanning interval of 0.2 nm, using the UV-1700 series instrument.

Computational methods

The entire quantum chemical calculations are performed on a Pentium IV/3.02 GHz personal computer using the Gaussian 09 software programs [6]. The calculated frequencies are scaled by suitable scale factors. The wave numbers and the geometry of the title molecule ISPB are computed using B3LYP functional and 6-311+G(d,p) [7] basis set and the same geometry is used for the

conformational analysis using semi-empirical method and PM6 basis set. The electronic properties, such as NBO and HOMO–LUMO were calculated using time-dependent TD-SCF – B3LYP method under the same basis set. Similarly the NMR chemical shifts are also carried out by GIAO method in combination with B3LYP/6-311G+(2d,p). In addition, the dipole moment, linear polarizability and the first order hyper polarizability of the title molecule are also computed using B3LYP method with the 6-311+G(d,p) basis set. The optimized structure of the molecule is shown Fig. 1.

Results and discussion

Potential energy surface (PES) scan

The conformational analysis of the molecule ISPB was performed by the potential energy surface (PES) scan function with the B3LYP/6-31++G(d,p) basis set by varying the dihedral angle 5C–12C–14C–18H in steps of 18° over one complete rotation 0–360 as recommended in the similar work [8]. The graphical result, total energy versus scan coordinate, of this conformer is presented in Fig. 2. The graph clearly shows that there are three minimum conformer at 60° , 180° and 300° with same energy $3.649 \times 10^{-23} \text{ kJ/mol}$. By which all these three conformers with the same minimum energy are the stable conformer of the compound.

The minimum energies obtained by the present study are much lower than the similar previous study by Fishman et al. [9]. The difference is due to usage of higher basis set in the present study which includes the corrected correlation in the many body system.

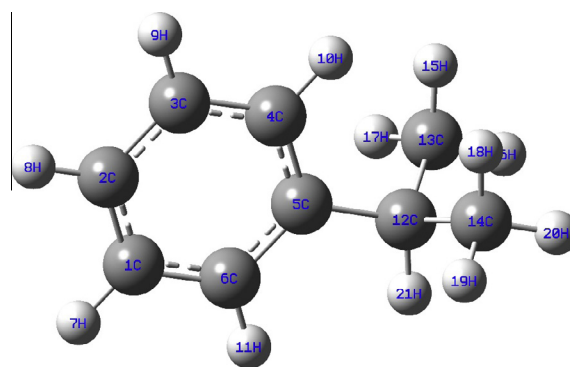


Fig. 1. Optimized structure of cumene.

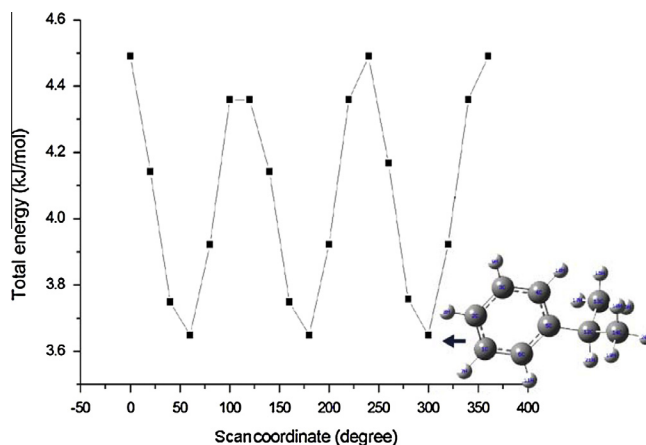


Fig. 2. Potential surface energy graph of cumene (dihedral angle –5C–12C–14C–18H).

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