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A theoretical density functional theory calculation-based analysis of conformers of *p*-xylene

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RESEARCH ARTICLE

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ABSTRACT

Different conformers of many aliphatic compounds such as ethane, butane, cyclohexane and their derivatives have been studied to find the most reactive as well as the most stable conformer. For the first time, two conformers of *p*-xylene were found using theoretical DFT calculation and the vibrational modes, Raman activity, and other spectra of each conformer were also studied. The most significant data that clearly distinguished both conformers was depolarization spectra. Besides, many other parameters were found different in both conformers of *p*-xylene such as Mulliken charge's, optimization energy, HOMO's of both conformers. Also, the presented study predicts, why eclipsed conformer of *p*-xylene is more reactive than staggered conformer. The reactivity of the eclipsed form is explained on the basis of HOMO-LUMO energy gap. Also, the presented study opens the door for future work to be done because each conformer can produce a specific product. Moreover, the rates of reaction are also dependent on the conformers and their relative stability.

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1. Introduction

Conformational isomers (conformers) are the isomers that have different orientations of atoms due to the rotation of the *sp*^{3}-hybridized centers. All conformers of a compound have a very small energy difference. The most stable conformer has lower energy than the less stable one. For example, the energy change between the two extreme conformers is about 12 kJ/mol in ethane [1]. Many research papers describing the conformational analysis in aliphatic compounds such as ethane-1,2-diol [2], 1,2-bis(*o*-carboxyphenoxy)ethane [3], *n*-butane and *n*-hexane [4] 1,4-dioxane [5], were appreciated. Besides, some other works have also been done on the derivatives of all types of xylene such as *o*-xylene [6], *m*-xylene [7], and *p*-xylene [8], but no paper regarding the underivatized *p*-xylene was found yet. Nobody developed an easy method that I did to determine the most stable conformer of *p*-xylene. There are many theoretical aspects to determine the conformers of a compound, theoretical DFT calculation is one of them. In the same way, there are many powerful tools and techniques to determine the conformers of a compound, vibrational spectroscopy is one of them [9,10]. Hence, the conformers of *p*-xylene were analyzed with the help of vibrational spectroscopy using a DFT calculation. Besides, the most important thing which cannot be denied, is the property of each conformer to produce a particular product by virtue of the Curtin-Hammett principle [11] because the rates of reaction depend on the conformers and their relative stabilities ruled by their strain [12]. A little bit of data regarding the dimethyl benzene was also found [13] but the work done was not sufficient especially for conformers of *p*-xylene. It is because the authors evaluated the conformers of only meta-xylene not that of *p*-xylene in their study. Besides, no depolarization data was given regarding the differences between conformers of *m*-xylene. Keeping this fact into consideration, the existence of conformers of *p*-xylene was studied. Besides, another most important thing to be kept in mind is the analysis of conformers on the basis of either unpolarized absorption (IR) or linearly polarized Raman spectra in the case of achiral molecules [14-19]. As per the literature survey, the depolarization spectra are one of the most significant tools for conformational analysis because each conformer has its unique depolarization spectra [14-19]. Hence, the depolarization spectra were generated for both conformers of *p*-xylene using DFT calculation. It is because DFT calculation has played an important role in the calculation of unpolarized absorption intensity and vibrational frequencies. Besides, density functional theory has significantly improved the correctness and competence of hypothetical methods [20-22].

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Figure 1. Structures of (a) eclipsed form and (b) staggered form of *p*-xylene.

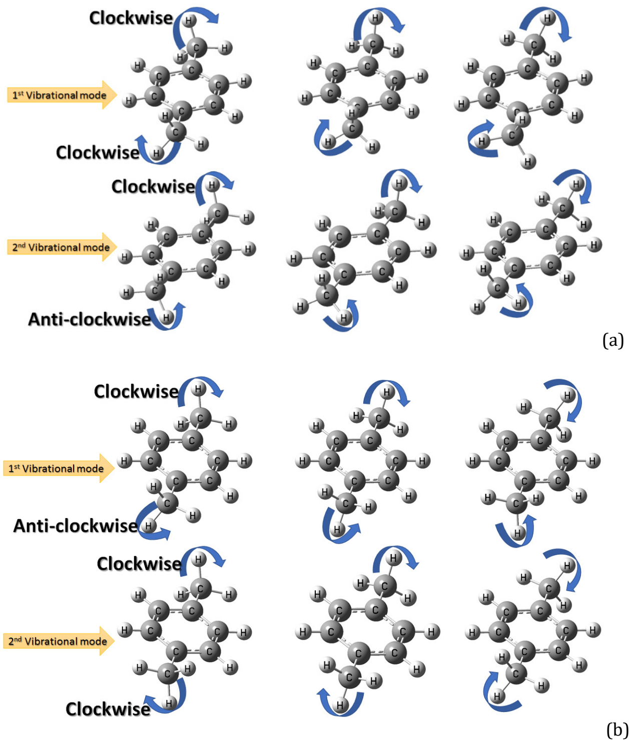

Figure 2. Vibrational modes of (a) eclipsed form (1st at 16.80 and 2nd at 33.25 cm^{-1}) and (b) staggered form (1st at 17.86 cm^{-1} and 2nd at 40.65 cm^{-1}).

In the presented paper, the capabilities of hypothetical DFT are illustrated via the conformation analysis of the achiral *p*-xylene.

2. Experimental

2.1. Software and tools

All software and tools used for the conformational analysis of *p*-xylene are MarvinSketch (16.9.12 version), Discovery studio, Gaussian(R) 03 program [23] and GaussView 6.0 [24].

2.2. Simulation method

The simulation study is very helpful in understanding the reaction mechanism [25-28], separation science [10,29-32], and the existence of conformers [33]. The presented study involved three important steps. The first step was to prepare MOL files of both conformers, the second was the calculation of different parameters of each conformer for the conformational analysis, and the final step was the analysis of data. First, the structures of both conformers i.e. eclipsed (Figure 1a) and staggered (Figure 1b) were drawn by MarvinSketch software and saved in "MOL file" format. The confirmation of the correctness of each structure was done using Discovery studio software. After that, the calculation for different parameters was done using Gaussian(R) 03 program. Finally, conformational analysis was done by GaussView 6.0.

In the presented study, the main parameters planned for the conformational analysis were vibrational modes with displacement vector, Raman spectrum, Depolarization spectra (P-Depolarization spectrum and U-Depolarization spectrum) of both conformers. Also, some other parameters were studied. Besides the optimization energy, the Mulliken's atomic charges in Coulomb's and Atomic Polar Tensor (APT) charges acquired by all atoms in both conformers (eclipsed and staggered) of *p*-xylene were also calculated by the DFT method in the ground state. Moreover, the difference in energy in HOMO of both conformers was also studied. The basis set used was 6-311++G(d,p) using Becke's three-parameter hybrid functionals [34] with Lee, Yang, and Parr correlation functional method (B3LYP) [35]. The interpretation in this study gave the distinguishable points between two conformers of *p*-xylene.

3. Results and discussion

3.1. Vibrational spectroscopic data

Both conformers showed 48 typed vibrational modes in which the first two vibrational modes of both conformers were different (Figure 2), while other types of vibrational modes were the same. The first two modes of the eclipsed form (Figure 2a) were different from those of the staggered form (Figure 2b). These results clearly showed the different behavior of each conformer in terms of vibrational modes.

Table 1. Theoretical DFT calculation-based variations found after optimization of conformers of *p*-xylene.

Parameters	Eclipsed	Staggered
E(RB+HF-LYP)	-310.96614 Hartree	-310.96615 Hartree
RMS gradient norm	2.9273×10^{-5} Hartree/Bohr	7.3311×10^{-5} Hartree/Bohr
Dipole moment	0.070008714 Debye	0.0032 Debye
Step number	8	7
Maximum force	9.2×10^{-5} Converged	0.000161 Converged
RMS force	1.5×10^{-5} Converged	3.7×10^{-5} Converged
Maximum displacement	0.000971 Converged	0.000937 Converged
RMS displacement	0.000326 Converged	0.000293 Converged
Predicted energy change	-8.100838×10^{-8} Hartree	-2.898959×10^{-7} Hartree

Table 2. Theoretical DFT calculation-based differences in physical properties of conformers of *p*-xylene.

Parameters	Eclipsed	Staggered
Polarizability	93.803 a.u.	93.917 a.u.
E (Thermal)	101.391 kcal/mol	101.977 kcal/mol
Heat Capacity (C_v)	27.429 cal/mol-kelvin	29.414 cal/mol-kelvin
Entropy (S)	85.04 cal/mol-kelvin	90.127 cal/mol-kelvin
Maximum force	9.6×10^{-5} Converged	0.000245 Converged
RMS force	2.9×10^{-5} Converged	7.5×10^{-5} Converged
Maximum displacement	0.033885 Not converged	0.0014 Converged
RMS displacement	0.000326-0.011897 Not converged	0.000542 Converged
Predicted energy change	-2.115147×10^{-7} Hartree	-3.069361×10^{-7} Hartree

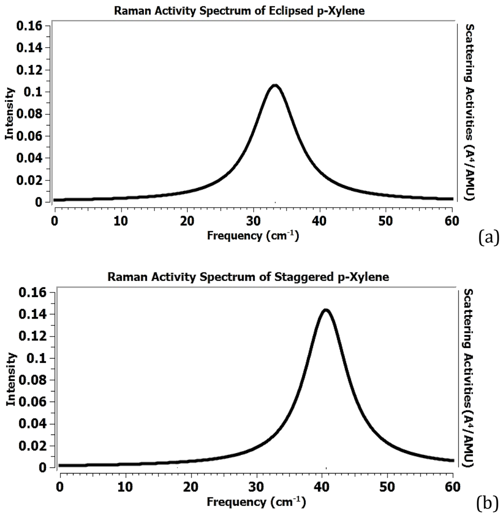

Figure 3. Raman activity spectrum of (a) eclipsed and (b) staggered form of *p*-xylene.

3.2. Raman spectrum

The Raman spectrum of both conformers of *p*-xylene was approximately the same, but a very small difference was found in the range of 30 to 50 cm^{-1} (Figure 3). This difference in data can also be used to distinguish between eclipsed and staggered forms of *p*-xylene. Besides, both conformers showed different Raman activity at 3018.83 cm^{-1}. It was 507.8020 $Å^4$/a.m.u. in the case of eclipsed form, and 538.7009 $Å^4$/a.m.u. in the case of staggered. No such distinguishable data was observed in the case of the IR spectrum of both conformers because it was almost the same for both conformers. Hence, both conformers were recognizable in the Raman spectrum but at very low frequency.

3.3. Depolarization spectra

Depolarization spectra (P-Depolarization spectrum and U-Depolarization spectrum) of both conformers of *p*-xylene were very much different (Figure 4), and gave the most significant information about the different behavior of both conformers. The depolarization spectra of the eclipsed form were very much different than those of staggered form, which can also be used to distinguish between eclipsed and staggered form. Hence, the obtained results were in full support of the literature data [14-19] according to which each conformer has its unique depolarization spectra. Although I studied and noted many important points differentiating each conformer from another one, these spectra had great importance for the current study. The major difference between the spectra of both conformers was found below the region of 1500 cm^{-1}. Above this region, the spectra of both conformers were approximately the same.

3.4. Optimization energy

After the calculation for optimization energies of both conformers, many differences between eclipsed and staggered forms of *p*-xylene were also observed, which were based on some important parameters mentioned in Table 1.

3.5. Charge distribution

Like other parameters, a variation of both charges (Mulliken and APT) on every atom in both conformers was also observed (Figure 5). Of course, this variation of charges can also be used to distinguish between the eclipsed and staggered form of *p*-xylene. A small change in charge was found on that carbon whose rotation gives rise to another conformer of *p*-xylene.

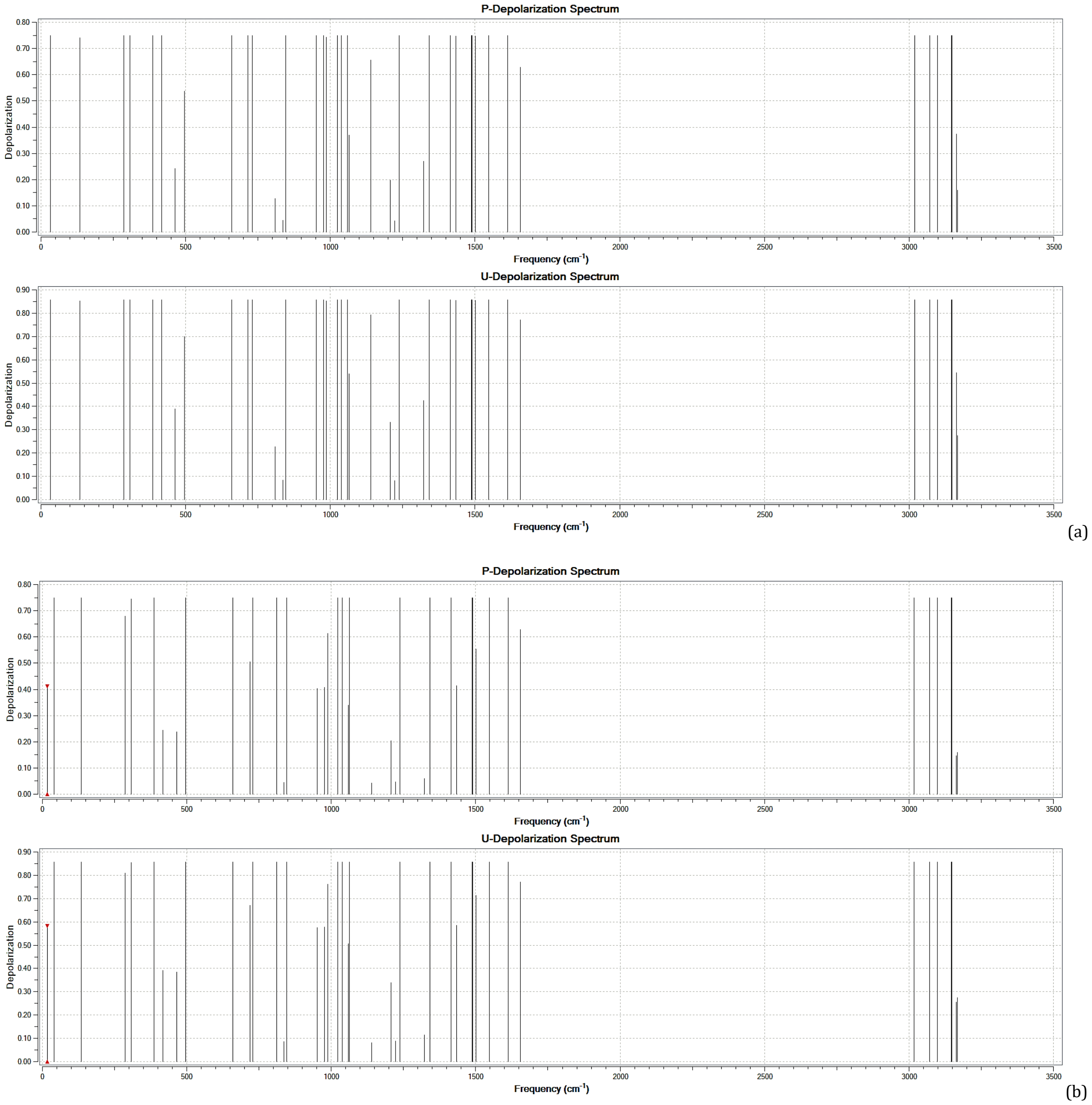

Figure 4. Depolarization spectra of (a) eclipsed and (b) staggered form of *p*-xylene.

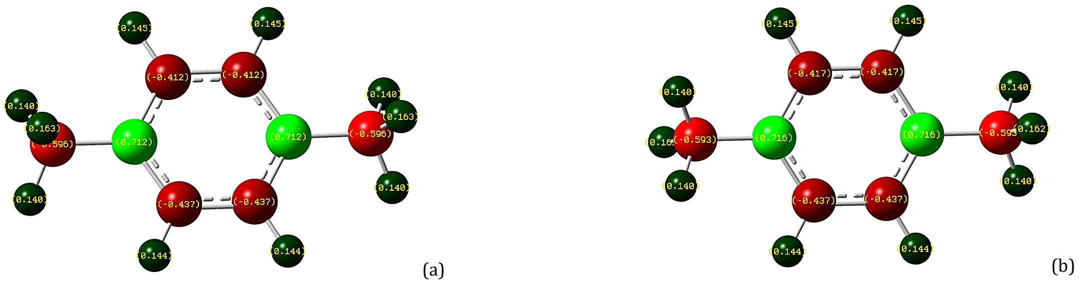

Figure 5. Mulliken atomic charges in (a) eclipsed form and (b) staggered form of *p*-xylene in coulombs.

3.6. HOMO-LUMO analysis

A difference in energy of HOMOs of both conformers was also observed as a distinguishable point between the two conformers. In both conformers, the energy difference between HOMO and LUMO of the staggered form was greater than that of the eclipsed form (Figure 6). Hence, the eclipsed form should be more reactive than the staggered form because it is very easy for the electron to enter into LUMO from HOMO in the case of eclipsed form. Therefore, we can say that a staggered form is more stable than eclipsed one.

3.7. Other parameters

Besides the conformational analysis-based computational data described above, some other differences were also found. These differences were based on some other parameters showing dissimilarities in both conformers (Table 2).

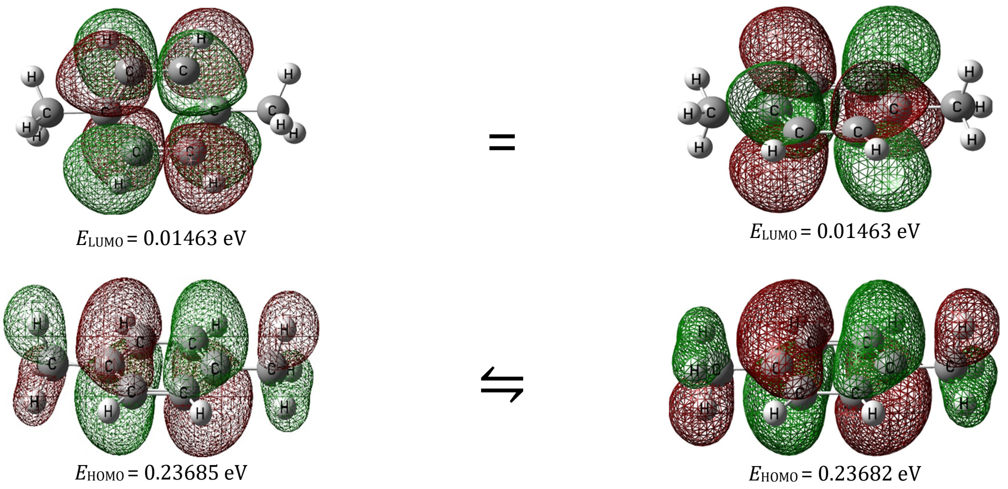

Figure 6. A HOMO-LUMO difference in the conformers of *p*-Xylene.

4. Conclusions

Based on results and discussion, it can be concluded that the observed theoretical data can be used to distinguish between eclipsed and staggered forms of *p*-xylene. Of course, the data of both conformers was different but the significant and distinguishable results were observed when the depolarization spectra of both conformers were observed. These distinguishable results were in full agreement with the literature data. Hence, the offered study may be suitable for the scientific community.

Disclosure statement

Conflict of interest: The author declares that he has no conflict of interest.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

CRediT authorship contribution statement

Conceptualization: Mohammad Suhail; Methodology: Mohammad Suhail; Software: Mohammad Suhail; Validation: Mohammad Suhail; Formal Analysis: Mohammad Suhail; Investigation: Mohammad Suhail; Resources: Mohammad Suhail; Data Curation: Mohammad Suhail; Writing – Original Draft: Mohammad Suhail; Writing - Review and Editing: Mohammad Suhail; Visualization: Mohammad Suhail; Funding acquisition: Mohammad Suhail; Supervision: Mohammad Suhail; Project Administration: Mohammad Suhail.

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