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Molecular Structure and TD-DFT Study of the Xylene Isomers

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Abstract

In this work, we have investigated the xylene isomers in concepts of vertical and adiabatic ionization energy parameters and molecular orbital (HOMO-1, HOMO/SOMO, LUMO, LUMO+1) energies of the neutrals and singly charged cation radicals. As a first step of the calculations, conformational analysis has been performed for all isomers using the semi-empirical method with PM3 core type Hamiltonian. Geometry optimization and frequency calculations were performed by using Density Functional Theory (DFT) with Becke, three-parameter, Lee-Yang-Parr (B3LYP) exchange-correlation functional and 6-311++G(d,p) basis sets. UV-Vis electronic spectra of the neutral xylene isomers were calculated by using the TD-DFT method with cam-B3LYP functional and 6-311++G(2d,2p) basis set.

1. INTRODUCTION

Xylene molecule is known as an aromatic hydrocarbon with three isomers of ortho-, meta-, and para-xylene (also named as; 1,2-Dimethylbenzene, 1,3-Dimethylbenzene and 1,4-Dimethylbenzene respectively). As a volatile organic compound (VOC), xylenes are classified as the BTEX (Benzene, Toluene, Ethylbenzene and Xylenes) group chemicals. BTEX compounds toxicological effects and interaction with those compounds were regulated [1]. In literature, some calculations for STO-3G level molecular structure for o-xylene were performed [2].

In the recent works, various theoretical calculations about to understand the structure of singlet and triplet states, and some experimental works to investigate electronic excitation and time-resolved relaxation dynamics were carried out on the o-xylene [3]. Furthermore fs-photoelectron imaging-photo fragmentation spectroscopy was used by the same group to reveal ultrafast dynamics of the cationic state of the o-xylene [4]. In addition, ring opening or isomerization mechanisms were investigated by using *ab-initio* methods to understand photoisomerization and photodissociation dynamics of the m-xylene [5]. Similar calculations were performed for o-xylene [6,7]. Experimentally two methyl group rotational dynamics of the o-xylene were investigated and found that dependence of the methyl rotor barrier and the ionization potential was lower than the o- and m-xylene [8]. Similar calculations were performed for three xylene isomers by using *ab-initio* method and HF/6-31(d) level theory [9]. Experimental and theoretical (6-31G** level) works on the vibronic properties of the ionic p-xylene molecule, and m-xylene [10], were given in literature [11]. In a recent work, intersystem crossing properties were investigated experimentally and theoretically [12] as well as due to vibrational and vibrational-torsional interactions [13,14].

In this work, we have investigated the neutrals and singly charged cation radicals of the xylene isomers in context of the vertical and adiabatic ionization energy parameters and molecular orbital (HOMO-1,

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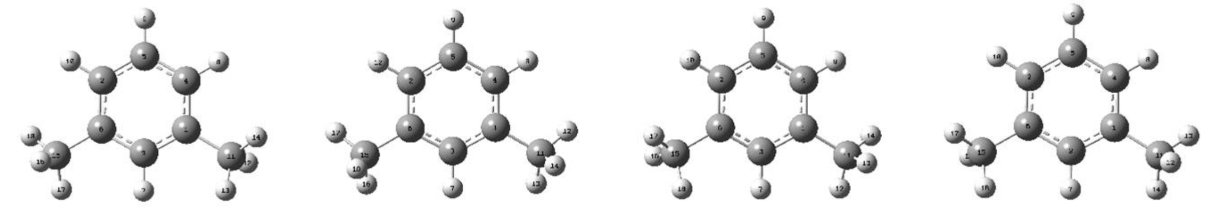
HOMO/SOMO, LUMO, LUMO+1) energies. In addition, UV-Vis spectra of the neutrals were also presented for three xylene isomers.

2. MATERIAL AND METHODS

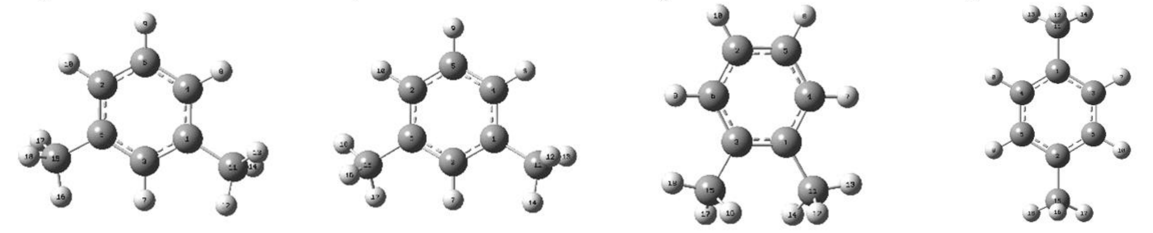
In the present paper, firstly, we have determined the most stable molecular conformation, the conformational analysis of isomers of the xylene molecule was performed using semi-empirical method PM3 core type Hamiltonian using the Spartan08 (Wavefunction Inc., Irvine, CA) program [15]. Subsequently, geometry optimizations and frequency analysis of the all possible conformers have been performed by B3LYP functional with 6-311++G(d,p) basis set by using Gaussian09 program [16]. Meta-xylene has six different conformers but only one conformer found for each of ortho- and para-xylene. Since, the most stable conformer of the isomers determined, singly charged cation radicals have been modelled and these have been used for the calculations of the vertical and adiabatic ionization energy parameters and molecular orbitals (HOMO-1, HOMO, LUMO, LUMO+1). Adiabatic ionization parameters were calculated by optimizing radical molecular geometry and the same molecular geometry as the neutral were used to calculate the vertical ionization parameters. UV-VIS electronic spectra of the neutral xylene isomers were calculated by using the TD-DFT method with cam-B3LYP/6-311++G(2d,2p) functional and basis set, respectively.

3. RESULTS

The conformational analysis has been performed as described in computational details section to investigate some properties of the xylene isomers. The conformational analysis shows that o- and p-xylene have one conformer while m-xylene has six conformers as seen in Figure 1. Molecular energies and dipole moment values of the conformers are given in Table 1. The fifth conformer of the m-xylene has a minimum energy corresponding to -310.9647576 Hartree. These minima for o- and p-xylene are -310.9657422 and -310.9661423 Hartree or -0.02679 eV and -0.03768 eV relative to the fifth conformer of the m-xylene. Dipole moment values have appeared as meta<ortho<para and given to be 0.3402, 0.6755 and 0.7060 Debye. We have found that stable ortho- and para-xylene consisted with previous works except meta-xylene differs from previous work that one methyl group rotated in 180° [9].



m-xylene Conformer 1 **m-xylene Conformer 2** **m-xylene Conformer 3** **m-xylene Conformer 4**



m-xylene Conformer 5 **m-xylene Conformer 6** **o-xylene** **p-xylene**

Figure 1. *Molecular conformer structures of the xylene isomers*

Table 1. *Energies and dipole moment values of the conformers of the Xylene isomers*

Isomers	**Energy (Hartree)**	**Relative Energy (Hartree)**	**Relative Energy (eV)**	**Relative Energy (kJ/mol)**	**Relative Energy (kcal/mol)**	**Relative Energy (cm^{-1})**	**Dipole Moment (D)**
m-xylene Conf5	-310.9647576	0.00000	0.00000	0.00000	0.00000	0.00000	0.3402
o-xylene	-310.9657422	-0.00098	-0.02679	-2.58499	-0.61783	-216.08358	0.6755
p-xylene	-310.9661423	-0.00138	-0.03768	-3.63569	-0.86895	-303.91328	0.7060
m-xylene Conf6	-310.9662373	-0.00148	-0.04027	-3.88490	-0.92851	-324.74537	0.3569
m-xylene Conf2	-310.9663249	-0.00157	-0.04265	-4.11510	-0.98353	-343.98850	0.3880
m-xylene Conf3	-310.9663268	-0.00157	-0.04270	-4.12007	-0.98472	-344.40330	0.3699
m-xylene Conf4	-310.9663269	-0.00157	-0.04271	-4.12033	-0.98478	-344.42524	0.3716
m-xylene Conf1	-310.9663270	-0.00157	-0.04271	-4.12054	-0.98483	-344.44280	0.3772

Table 2. *HOMO-LUMO and Bandgap values of the neutral xylene isomers*

Isomers	E_{LUMO} **(a.u.)**	E_{LUMO} **(eV)**	E_{HOMO} **(a.u)**	E_{HOMO} **(eV)**	E_{gap} **(a.u)**	E_{gap} **(eV)**
m-xylene	-0.23915	-6.5077498	-0.01346	-0.36627352	-0.22569	-6.14147628
o-xylene	-0.24113	-6.56162956	-0.01061	-0.28871932	-0.23052	-6.27291024
p-xylene	-0.23682	-6.44434584	-0.01462	-0.39783944	-0.22220	-6.04650640

HOMO-LUMO energies (a.u. and as eV unit) and the HOMO-LUMO energy gap values have given in Table 2 for the ground state neutral molecules. Energy gap values increase in the order ortho>meta>para. Neutral molecules HOMO-1, HOMO, LUMO and LUMO+1 orbitals presented in Figure 2. As shown in Figure 2, molecules exhibit π-type bonding. After geometry optimizations and frequency calculations, ionisation properties of the isomers have been investigated theoretically by means of the vertical and adiabatic process by removing one electron (charge: +1, multiplicity: 2). In order to calculate adiabatic ionization, an additional step (geometry optimization) have performed to simulate adiabatic relaxation to minimum molecular energy level. In contrast, for calculating vertically ionized molecules, its neutral geometries were used. HOMO-1, HOMO, LUMO and LUMO+1 orbitals of the adiabatically and vertically ionized molecules are presented in FigureS 3 and 4, respectively.

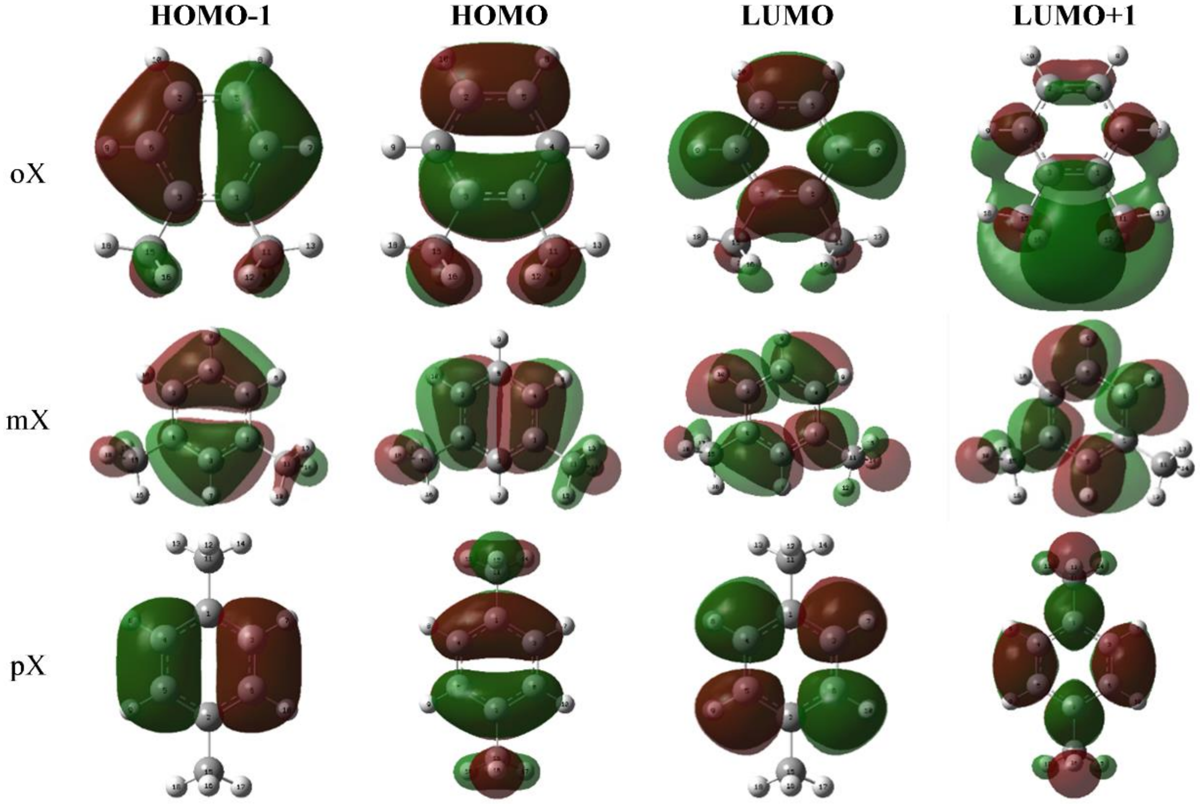


Figure 2. *Molecular orbitals of the stable conformer of the xylene isomers*

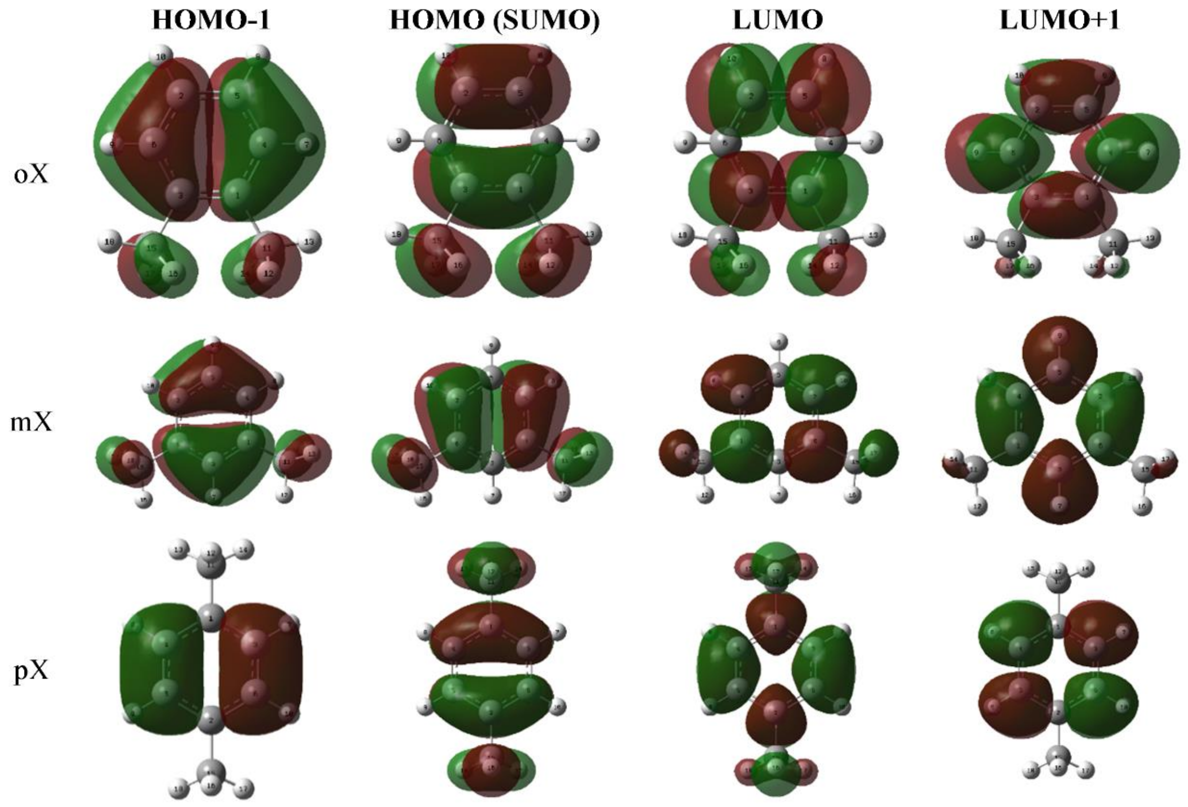


Figure 3. *Molecular orbitals of the radicals (adiabatically ionised molecule)*

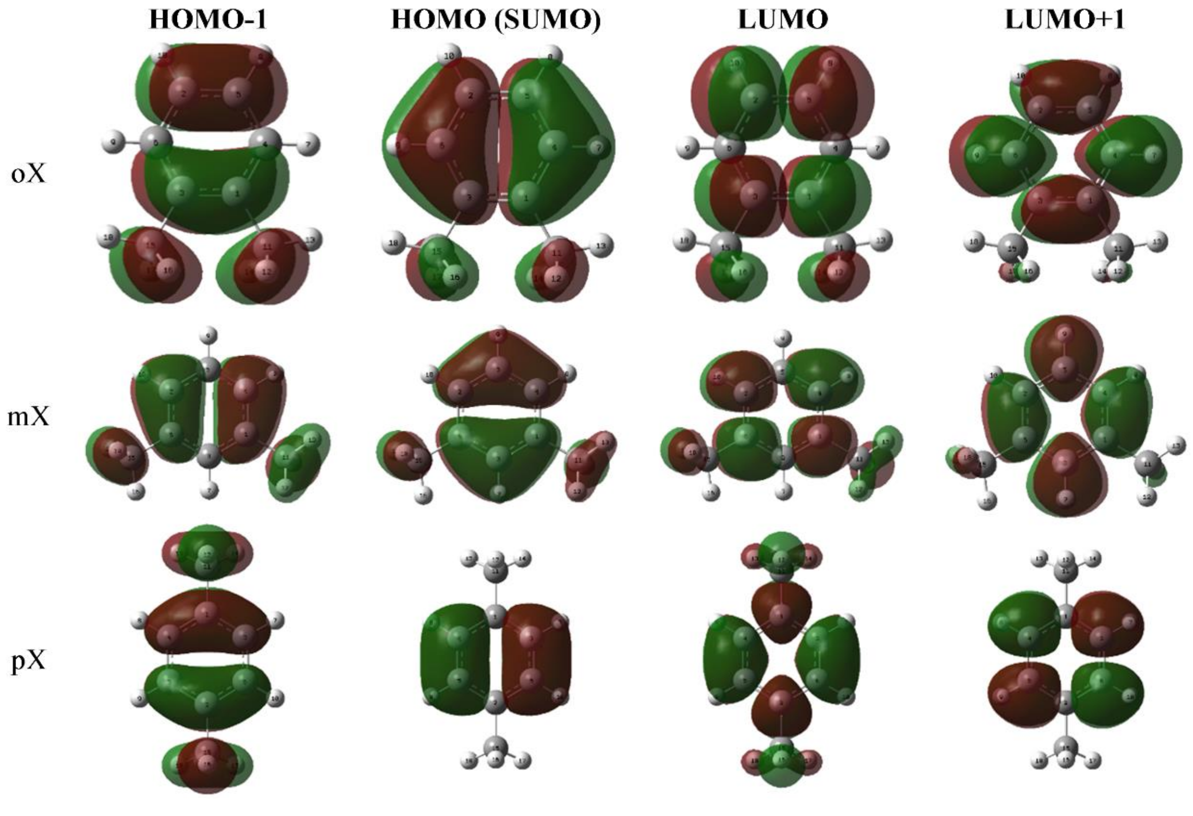


Figure 4. *Molecular orbitals of the radicals (vertically ionised molecule)*

Calculated molecular energies, relative energies to its neutrals and dipole moments are presented in Table 3 as well as energy diagrams of the xylene isomers are given in Figure 5. HOMO-LUMO energies (a.u. and as eV unit) and the HOMO-LUMO energy gap values have been given in Table 4 for the vertically and adiabatically ionized molecules.

Adiabatically ionized o-, m- and p-xylene have minimum energies corresponding to -310.6575548, -310.659618 and -310.6634675 Hartree or 0.30818739, 0.30513955 and 0.30267482 Hartree relative to their neutrals. Vertically ionized o-xylene, m- and p-xylene have minimum energies corresponding to -310.6517349 Hartree, -310.652897 and -310.656973 Hartree, respectively, and these are lower in the amount of 0.3140072, 0.31186055 and 0.30916866 Hartree than their neutrals, respectively.

In contrast to its neutral, dipole moment values appear as para<ortho<meta for both adiabatically and vertically ionized molecules.

Energy diagram of the isomers are presented in Figure 5 shows that the neutral molecular energies for isomers increase in order of meta<ortho<para when they lose one of their electrons (i.e. after ionization), this trend changes to the order of para<meta<ortho for both electron loss mechanism (Vertical or Adiabatic). As expected, adiabatic energy levels are lying lower than the vertical molecular energy levels.

Table 3. *Molecular energies (relative to its neutrals) and dipole moments of the xylene isomers (AI: Adiabatic Ionization, VI: Vertical Ionization)*

Isomers	**Energy (Hartree)**	**Relative Energy (Hartree)**	**Relative Energy (eV)**	**Relative Energy (kJ/mol)**	**Relative Energy (kcal/mol)**	**Relative Energy (cm^{-1})**	**Dipole Moment (D)**
m-xylene (AI)	-310.659618	0.30513955	8.303457435	801.1438885	191.478119	66968.97704	0.6294
o-xylene (AI)	-310.6575548	0.30818739	8.386395257	809.1459924	193.3906691	67637.88648	0.3009
p-xylene (AI)	-310.6634675	0.30267482	8.236387202	794.6727399	189.9314763	66428.04275	0.2767
m-xylene (VI)	-310.652897	0.31186055	8.486349287	818.789874	195.6956137	68444.03491	0.5645
o-xylene (VI)	-310.6517349	0.31400727	8.544765831	824.4260874	197.042702	68915.17555	0.4602
p-xylene (VI)	-310.6569737	0.30916866	8.413097576	811.7223168	194.0064258	67853.24581	0.1885

Table 4. *HOMO-LUMO energies and Bandgap values of the xylene isomers*

Isomers	E_{LUMO} ***(a.u.)***	E_{LUMO} ***(eV)***	E_{HOMO} ***(a.u)***	E_{HOMO} ***(eV)***	E_{gap} ***(a.u)***	E_{gap} ***(eV)***
m-xylene	-0.24063	-6.54802356	-0.45905	-12.4916686	0.21842	5.94364504
o-xylene	-0.23931	-6.51210372	-0.45947	-12.50309764	0.22016	5.99099392
p-xylene	-0.23355	-6.3553626	-0.46423	-12.63262676	0.23068	6.27726416
m-xylene	-0.23024	-6.26529088	-0.46921	-12.76814252	0.23897	6.50285164
o-xylene	-0.23137	-6.29604044	-0.47062	-12.80651144	0.23925	6.510471
p-xylene	-0.22586	-6.14610232	-0.46133	-12.55371196	0.23547	6.40760964

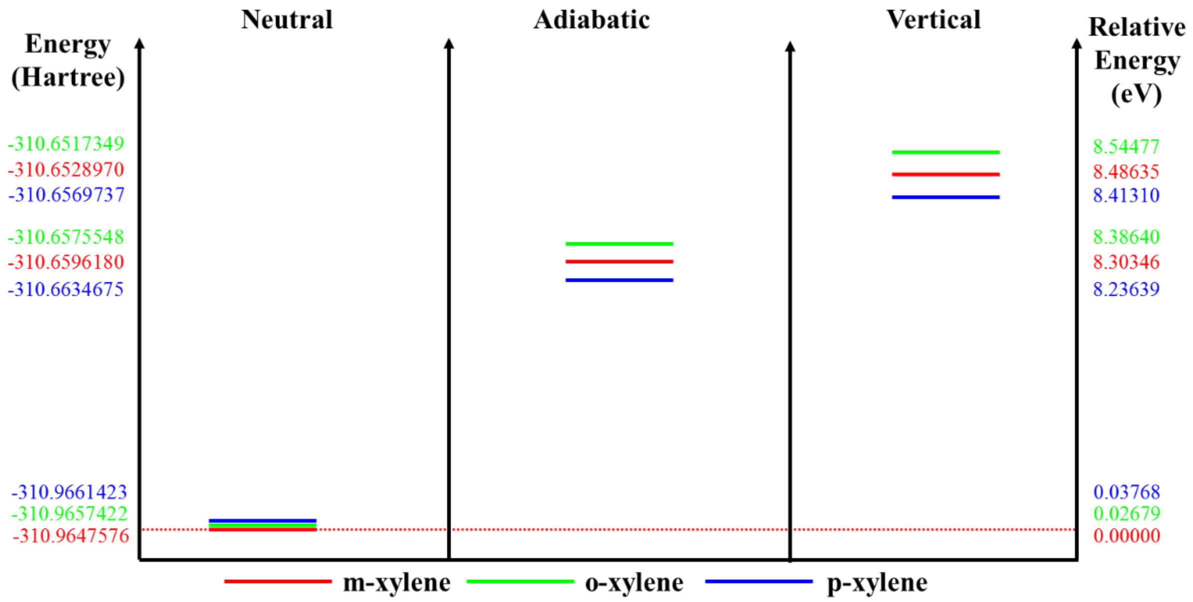


Figure 5. *Energy diagram of the xylene isomers (energies relative to the neutral molecular energy)*

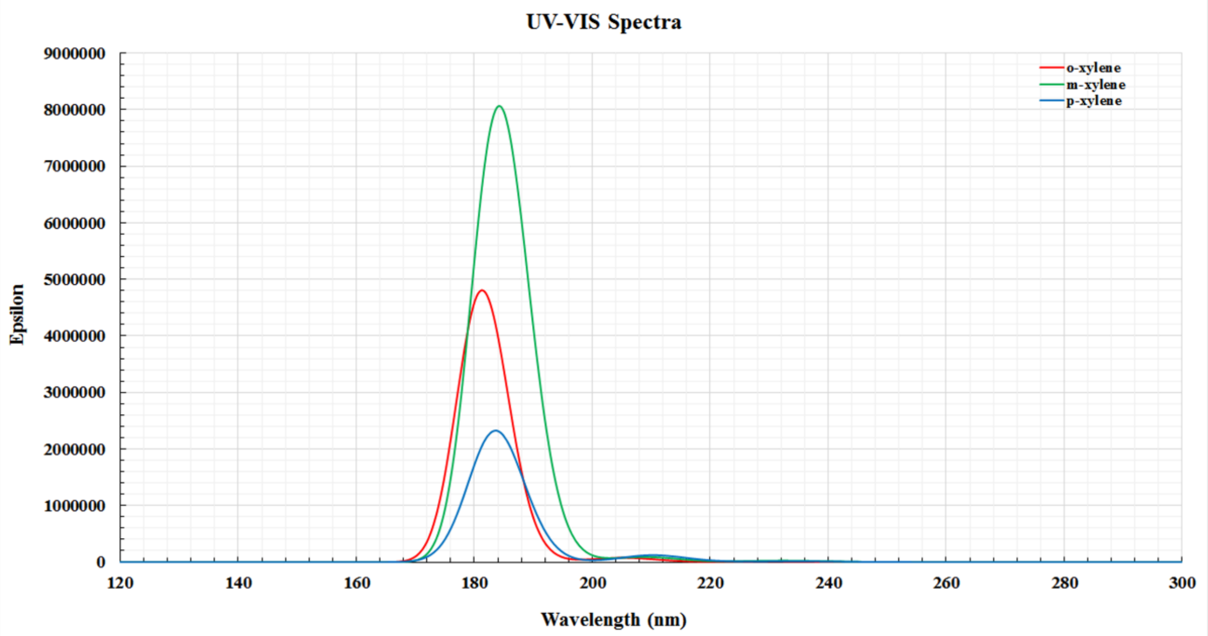


Figure 6. *Calculated UV-Vis spectra of the xylene isomers (GaussSum* [17] *program was used to plot spectra)*

UV-Vis spectra of the xylene isomers are presented in Figure 6. All isomers have a strong absorption band around 180 nm and relatively small absorption band around 210 nm are observed due to calculation results. Major contributions to the UV-Vis spectra and corresponding transitions are presented in Table 5 to 7.

For the o-xylene isomer, leading contributions to UV-Vis spectrum originated from HOMO-1→LUMO+4 (54%), HOMO→LUMO+3 (43%) transitions with 6.8826 eV energy gap, HOMO-1→LUMO+2 (87%) transition with 6.8257 eV energy gap and HOMO-1→LUMO+3 (58%), HOMO→LUMO+4 (37%) transitions with 6.7939 eV energy gap values.

In the matter of m-xylene isomer, leading contributions to UV-Vis spectrum originated from HOMO-1→LUMO+4 (58%) and HOMO→LUMO+3 (33%) transitions with 6.7899eV energy gap, HOMO-1→LUMO+3 (38%), HOMO→LUMO+2 (18%) and HOMO→LUMO+4 (32%) transitions with 6.6496eV energy gap and HOMO-1→LUMO+3 (12%), HOMO→LUMO+2 (61%) transitions with 6.6282eV energy gap values.

In case of the p-xylene isomer, leading contributions to UV-Vis spectrum originated from HOMO-1→LUMO+4 (63%), HOMO→LUMO+3 (33%) transitions with corresponding to 6.7968 eV energy gap, HOMO-1→LUMO+3 (68%), HOMO→LUMO+4 (27%) transitions with 6.6729 eV energy gap values.

Table 5. *TD-DFT results for the excited states of the neutral o-xylene isomer (f is the oscillator strength)*

Excited State	*ΔE (eV)*	*ΔE (nm)*	*f*	**Major Contributions to the Transitions (percentage)**
1	5.3952	229.8046	0.0024	HOMO-1→LUMO+4 (41%), HOMO→LUMO+3 (50%)
2	6.0168	206.0633	0.0107	HOMO-1→LUMO+3 (36%), HOMO→LUMO+4 (59%)
3	6.0871	203.6835	0.0089	HOMO→LUMO (88%)
4	6.3381	195.6173	0.0000	HOMO-1→LUMO (79%), HOMO-1→LUMO+1 (11%)
5	6.4711	191.5968	0.0024	HOMO→LUMO+1 (90%)
6	6.6796	185.6162	0.0000	HOMO-1→LUMO+1 (11%), HOMO→LUMO+2 (83%)
7	6.7939	182.4934	0.4973	HOMO-1→LUMO+3 (58%), HOMO→LUMO+4 (37%)
8	6.8257	181.6432	0.0218	HOMO-1→LUMO+2 (87%)
9	6.8375	181.3297	0.0000	HOMO-1->LUMO (11%), HOMO-1→LUMO+1 (72%), HOMO->LUMO+2 (10%)
10	6.8826	180.1415	0.7328	HOMO-1→LUMO+4 (54%), HOMO→LUMO+3 (43%)

Table 6. *TD-DFT results for the excited states of the neutral m-xylene isomer (f is the oscillator strength)*

Excited State	*ΔE (eV)*	*ΔE (nm)*	*f*	**Major Contributions to the Transitions (percentage)**
1	5.3387	232.2367	0.0033	HOMO-1→LUMO+3 (11%), HOMO-1→LUMO+4 (25%), HOMO→LUMO+3 (41%), HOMO→LUMO+4 (11%)
2	5.9371	208.8296	0.0112	HOMO-1→LUMO+3 (32%), HOMO→LUMO+3 (17%), HOMO→LUMO+4 (37%)
3	6.0983	203.3094	0.0000	HOMO→LUMO (88%)
4	6.3239	196.0565	0.0031	HOMO-1→LUMO (88%)
5	6.5916	188.0942	0.0061	HOMO→LUMO+1 (74%)
6	6.6282	187.0556	0.1001	HOMO-1→LUMO+3 (12%), HOMO→LUMO+2 (61%)
7	6.6496	186.4536	0.3292	HOMO-1→LUMO+3 (38%), HOMO→LUMO+2 (18%), HOMO→LUMO+4 (32%)
8	6.7899	182.6009	0.6726	HOMO-1→LUMO+4 (58%), HOMO→LUMO+3 (33%)
9	6.7984	182.3726	0.0210	HOMO-1→LUMO+2 (82%)
10	6.9633	178.0538	0.0001	HOMO-1→LUMO+1 (89%)

Table 7. *TD-DFT results for the excited states of the neutral p-xylene isomer (f is the oscillator strength)*

Excited State	*ΔE (eV)*	*ΔE (nm)*	*f*	**Major Contributions to the Transitions (percentage)**
1	5.2920	234.2861	0.0064	HOMO-1→LUMO+3 (23%), HOMO→LUMO+4 (68%)
2	5.9032	210.0288	0.0495	HOMO-1→LUMO+4 (29%), HOMO→LUMO+3 (61%)
3	5.9888	207.0268	0.0003	HOMO→LUMO (91%)
4	6.4409	192.4951	0.0001	HOMO→LUMO+1 (93%)
5	6.4555	192.0598	0.0001	HOMO-1→LUMO (88%)
6	6.5428	189.4971	0.0000	HOMO→LUMO+2 (95%)
7	6.6729	185.8026	0.3594	HOMO-1→LUMO+3 (68%), HOMO→LUMO+4 (27%)
8	6.7968	182.4155	0.6246	HOMO-1→LUMO+4 (63%), HOMO→LUMO+3 (33%)
9	6.9216	179.1265	0.0328	HOMO-1→LUMO+2 (92%)
10	7.0189	176.6433	0.0301	HOMO→LUMO+5 (88%)

4. CONCLUSION

In this study, TD-DFT calculations for xylene isomers are discussed in details to reveal effect of the relative positions of the methyl groups. Conformational analysis indicates that molecular geometries of the stable ortho- and para-xylene consisted with literature except for meta-xylene, which differs from literature that one methyl group rotated in 180°. Since the conformational analysis has been applied for xylene isomers, the vertical and adiabatic ionization energy parameters and molecular orbital (HOMO-1, HOMO/SOMO, LUMO, LUMO+1) energies of the neutrals and singly charged cation radicals have been calculated, respectively. The neutral molecular energies and the bandgap values of the conformers increase in the order ortho>meta>para and theoretical calculations shown that this trend changes to the order of para<meta<ortho for both electron loss mechanism (Vertical or Adiabatic). First ten excited states energies and oscillator strengths as well as corresponding UV-Vis spectra have been presented for three xylene isomers.

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CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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