Heliyon 6 (2020) e04957

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Research article

Theoretical study of internal rotational barriers of electrons donating and electrons withdrawing groups in aromatic compounds

Daniel Rodrigues Lima [a], Sílvio Quintino de Aguiar Filho [a], Laura Beatriz Camargo do Oh [a], Anna Karla dos Santos Pereira [b], Douglas Henrique Pereira [a,*]

[a] *Chemistry Collegiate, Federal University of Tocantins, Campus Gurupi -Badejós, P.O. Box, 66, 77 402-970, Gurupi, Brazil*
[b] *Institute of Chemistry, University of Campinas – UNICAMP, PO Box 6154, 13083-970, Campinas, SP, Brazil*

ARTICLE INFO

Keywords:
Organic chemistry
Theoretical chemistry
Stereoelectronic effects
QTAIM
NBO
Free rotor

ABSTRACT

The presence of internal rotation in sigma bonds is essential for conformational analysis of organic molecules and its understanding is of great relevance in chemistry, as well as in several other areas. However, for aromatic compounds that have substituent groups, withdrawers or donors of electron, there are no data in the literature to explain their rotational barriers. In this context, the work studied the internal rotational barriers of electron donating and withdrawing groups in aromatic compounds using the MP3, MP4, and CCSD(T) methods and the influence of substituents' nature on barrier heights was investigated through calculations based on the theory of Natural Bond Orbitals (NBO) and Quantum Theory of Atoms in Molecules (QTAIM). The results obtained showed that the CCSD(T) method is the one that best describes the internal rotational barriers, followed by MP4 and MP3 and the electron donating groups decrease the barrier, whereas electron withdrawing groups increase. Through the NBO analysis it was possible to observe that for withdrawing groups the interaction of the molecular orbitals is more accentuated promoting the increase of the rotational barrier of these compounds. Through the QTAIM analysis it was possible to show that, for electron donating groups, the internal rotation is influenced by the loss of electronic density when the substituents is perpendicular to the ring plane, however, for withdrawing groups the density is little influenced, regardless of the two conformations (minimum and maximum energy). Two molecules showed free rotation, trichloromethylbenzene and methylbenzene, and the theoretical calculations NBO and QTAIM showed that for these species there is no difference in the properties studied when there is rotation of the dihedral angle.

1. Introduction

Atoms and/or groups of atoms bonded to aromatic compounds are classified as electron donating or withdrawing groups and are extremely important in the study of organic chemistry [1, 2, 3, 4]. The addition of groups to the aromatic ring causes changes in stability, reactivity and reaction rate [1, 2, 3]. The presence of an electron withdrawing group causes an increase in the energy of the state transition when compared to benzene in an electrophilic substitution reaction. On the other hand, a donating group causes a decrease in the energy of the state transition when compared to benzene in an electrophilic substitution reaction [1, 2, 3, 4].

Aromatic compounds have numerous applications, such as in drug synthesis, polymer formation, explosives manufacturing, vitamin composition, among others [1, 2, 3, 4]. Therefore, rotational barrier studies are good tools for to understand the conformational changes that are closely related to problems of great importance in the areas of chemistry, biology and biochemistry [5, 6, 7, 8, 9, 10].

In the experimental context, spectroscopic techniques with an emphasis on Raman spectroscopy, crystallography and microwave spectroscopy are the most used techniques to analyze the probable conformations of molecules of interest and then determine the values of rotational barriers [11, 12, 13]. On the other hand, computational studies have been frequently found in the literature, looking for elucidate the stereoelectronic effects responsible for the most stable conformations of different systems [14, 15].

In this context, several studies have been reported in the literature related to the rotational barrier of substituents in aromatic compounds [16, 17, 18, 19, 20]. The works already reported bring innumerable importance and allow the understanding of the stereoelectronic effects of

---

* Corresponding author.
E-mail address: doug@uft.edu.br (D.H. Pereira).

https://doi.org/10.1016/j.heliyon.2020.e04957
Received 8 July 2020; Received in revised form 3 August 2020; Accepted 14 September 2020

the most different substituents, such as the work of Cimiraglia and Hofmann (1994) [17], who investigated the relationship between the rotation and inversion mechanisms in the E/Z isomerization of the N-phenyldiazene and azobenzene compounds. P. C. Chen and S. C. Chen (2001) [18], studied the compounds of nitrobenzene, 2-nitrophenol, 2-nitroaniline, 2-nitrotoluene and 2-nitrophenol identifying the main stereoelectronic effects responsible for the rotation of nitrogen groups.

Although several studies are reported in the literature on substituents and their rotations, there is no evidence of differences in stereoelectronic properties between electron donating and withdrawing groups so far. Therefore, the present work aims to study the stereoelectronic effects responsible for the heights of the internal rotational barriers of a series of electron donating and withdrawing groups in aromatic compounds.

2. Computational details

All compounds were optimized to the minimum of energy using the MP2 method with the basis set 6-311++G (2df,p). The basis set 6-311++G (2df,p) was chosen because describes well the atoms present in the compounds and that presents computational cost limited. The potential energy surfaces describing the internal rotations of the various compounds under exam have been calculated at the MP2/6-311++G (2df,p) level. In order to increase electronic correlation single point calculations were used with different methods to determine the profile of the internal rational barriers which were MP3, MP4 and CCSD(T). It is important to highlight that the structures were not optimized at the MP3, MP4 and CCSD(T) levels due to the high computational cost.

The methodology of Natural Bond Orbitals (NBO) at CCSD(T)/6-311++G (2df,p) level was used to evaluate the interactions of bonding and antibonding orbitals between the substituents and the aromatic ring [21]. Topological analyzes of the internal rotational barriers of the molecules were performed using the Quantum Theory of Atoms in Molecules (QTAIM) [22, 23, 24] at the MP2/6-311++G (2df,p) level. The topological properties analyzed for the system were electronic density (ρ(r)), the laplacian of the electronic density ($\nabla^2\rho$(r)) and the ellipticity (ε(r)), at Bond Critical Points (BCP) [22, 23, 24]. According to QTAIM, ρ(r) corresponds the chemical bond strength, for laplacian of the electronic density the values of $\nabla^2\rho(r) < 0$ indicate covalent bonds and $\nabla^2\rho(r) > 0$ indicate non-covalent bonds. The values of $\varepsilon(r) = 0$ indicates that the bond is essentially σ and the greater the value of ε(r) the greater the π character of a bond.

For the calculations of electronic structure QTAIM and NBO, relaxed structures were used. QTAIM analyses were performed using the AIMALL package [25]. All other calculations were performed using the Gaussian 09 program [26].

3. Results and discussion

The employed computational methods MP3, MP4 and CCSD(T) and the NBO and QTAIM analyzes were used to understand the stereoelectronic effects of the internal rotational barriers of electron donating and withdrawing groups in aromatic compounds. Four electron donating groups and four electron withdrawing groups were studied and the choice of systems occurred because the rotational barriers present experimental values reported in the literature. Figure 1 shown all the

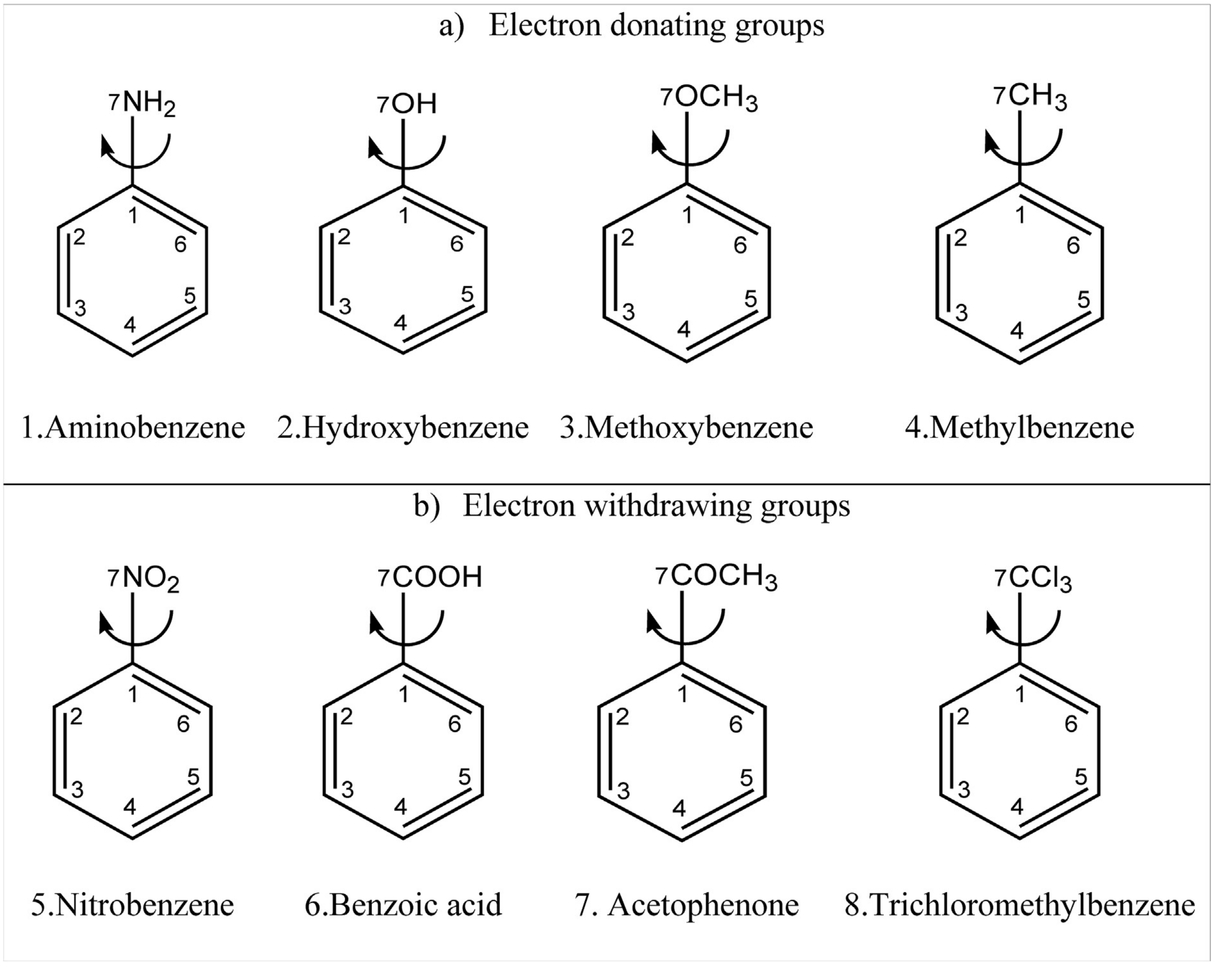

Figure 1. Molecule structures studied and their torsion angle around the dihedral angle with respect to the aromatic ring for: a) electron donating groups and b) electron withdrawing groups.

structures studied and the torsion dihedral angle of the substituent. For all compounds, the dihedrals angles varied from 0° to 180° in 10° intervals and the initial dihedral angle was 0° for all scans.

3.1. Internal rotational barriers

The experimental values found in the literature and theoretical values of the internal rotational barriers for the structures, $C_6H_5NH_2$, C_6H_5OH, $C_6H_5OCH_3$, $C_6H_5CH_3$, $C_6H_5NO_2$, C_6H_5COOH, $C_6H_5C(O)CH_3$, and $C_6H_5CCl_3$ are shown in Table 1. The values for deviations from calculated values and experimental values are shown in parentheses and were calculated by the difference between experimental and theoretical values, $\Delta E_{dev} = \Delta E_{exp} - \Delta E_{calc}$. A relative difference allows a better response to the error associated with the calculation methodology of each method. The mean absolute error (MAE) was calculated using Eq. (1).

$$MAE = \left(\sum_{k=1}^{N} |x_{ik} - x_{jk}| \right) \Big/ N \tag{1}$$

x_{ik} is the experimental value and x_{jk} is the calculated value. The MAE values are shown in the last line of Table 1.

When comparing the methods used to calculate the rotational barriers of aromatic compounds, it was found that the CCSD(T) method is the most accurate with MAE of 0.49 kcal mol^{-1}, followed by MP4 and MP3 with MAE of 0.55 kcal mol^{-1} and 0.64 kcal mol^{-1}, respectively. The MAE results follows the expected order for the accuracy and computational cost of the methods. It is worth noting that the MAE for all methods was small, thus showing the accuracy of the calculations employed.

Analyzing the theoretical error found for each structure individually, it is possible to observe that aminobenzene and benzoic acid showed high errors for all calculations used.

Another important point to note is that the heights of the rotational barriers for the withdrawing groups are greater in relation to the height of the barriers of the donating groups. In this context two molecules are exceptions, which are the methylbenzene and trichloromethylbenzene. These compounds present experimental rotational barriers close to zero with values of 0.03 and 0.30 kcal mol^{-1} [29,34], respectively, showing that the resistance to turning around the C–C bond is minimal, thus characterizing a free rotation at room temperature (RT = 0.60 kcal mol^{-1}).

Figure 2 plots the rotational barriers of all studied molecules. For compounds C_6H_5OH, $C_6H_5OCH_3$, C_6H_5COOH, $C_6H_5C(O)CH_3$ and $C_6H_5NO_2$ the rotational barrier profiles show the formation of more stable conformers at 0° and 180°, that is, when the substituent is in the plane of the ring, and separated by an energy maximum at 90° when the substituent is perpendicular to the plane of the ring. For the compound $C_6H_5NH_2$ the profile shows the formation of more stable conformers at 30° and lesser at 120°.

One can note that the potential energy surface of the $C_6H_5CH_3$ compound shown three equivalent minima at 30°, 90° and 150° and three equivalent maxima at 60°, 120° and 180°, whereas $C_6H_5CCl_3$ presents stable conformers for the dihedral angles at 0°, 60°, 120° and 180°, exhibiting energy maxima at 30°, 90° and 120°.

From the results described by the rotational barriers it is possible to infer that: i) electrons donating groups have lower rotational barriers than electrons withdrawing groups; ii) some structures have free rotation. With the results of the trends of the rotational barriers found, i) and ii), the NBO and QTAIM methodologies were applied to understand the stereoelectronic effects that justify the results.

3.2. Natural Bond Orbitals– NBO

The Natural Orbital Orbitals is important for determining the stability of a chemical bond through the energy eigenvalues of the bonding orbitals, where the energy of the orbitals is calculated by determining second order perturbation energy (ΔE^2) [21]. In this context, the NBO analysis was applied in order to assess the main interactions that occur between formally occupied and unoccupied NBO for the conformations that appear in the minimum and maximum energy.

Three systems, hydrobenzene, benzoic acid, methylbenzene, showing an electrons donating group, an electrons withdrawing group and a free rotor group, respectively, have been evaluated (Tables 2, 3, and 4). The other systems are reported in the supplementary material, Tables S1-S5. For all molecules, only the NBO analyses between the substituent with the aromatic ring were evaluated and only interactions with second order perturbation energy ($\Delta E^{(2)}$) above 3.00 kcal mol^{-1} were analyzed.

The results for hydroxybenzene are shown in Table 2 and it is observed that when the substituent is in the plane of the aromatic ring, at 0°, there is a strong interaction between the bonding pi orbital (π) with antibonding pi orbital (π^*) (n π O12 $\rightarrow$ π^* C1–C2) with energy value of 34.52 kcal mol^{-1}. This high energy value corresponds to the resonance that occurs between the substituent and the aromatic ring.

However, when the substituent is perpendicular to the plane of the aromatic ring, at 90°, it is noted that the number of interactions between the orbitals increases, but the energy values decrease significantly, as a result of the less overlap of the resonant orbitals. The greater number of interactions between NBO at 90° can be explained by the interaction of the substituents with the other ring atoms. It is worth noting that the other donating groups follow the same trend, Tables S1 and S2 supplementary material.

The results of the NBO for benzoic acid are shown in Table 3. The data show that the difference between the 0° and 90° conformer is in the fact that in 0° the energy values of the NBOs are greater than in 90°. The results also show that for the electron withdrawing group, the NBO found have high values of $\Delta E^{(2)}$ mainly for interactions: π^* C5 – C6$\rightarrow$$\pi^*$ C12 – O13, n π O14$\rightarrow$$\pi^*$ C12 – O13 and n π O13$\rightarrow$$\sigma^*$ C12 – O14. The values of the orbital interactions justify the greater rotational barriers of the

Table 1. Experimental, theoretical values and relative error between parentheses for the internal rotational barriers calculated with the MP3, MP4 and CCSD(T) methods and the 6-311++G (2df, p) basis set. Data in kcal mol^{-1}.

Molecules	Exp.	Ref.	MP3	MP4	CCSD(T)
Electron donating groups					
$C_6H_5NH_2$	3.50	[27]	4.43 (-0.93)	4.51 (+1.02)	4.55 (+1.05)
C_6H_5OH	3.47	[28]	2.98 (+0.49)	3.15 (+0.32)	3.24 (+0.23)
$C_6H_5CH_3$	0.03	[29]	0.05 (-0.02)	0.04 (-0.01)	0.05 (-0.02)
$C_6H_5OCH_3$	3.60	[30]	2.35 (+1.25)	2.59 (+1.01)	2.67 (+0.93)
Electron withdrawing groups					
C_6H_5COOH	5.10	[31]	6.43 (-1.33)	6.01 (-0.91)	6.08 (-0.98)
$C_6H_5C(O)CH_3$	5.40	[32]	5.23 (+0.17)	4.83 (+0.57)	5.10 (+0.30)
$C_6H_5NO_2$	4.56	[33]	5.42 (-0.86)	4.83 (-0.27)	4.88 (-0.32)
$C_6H_5CCl_3$	0.30	[34]	0.19 (+0.11)	0.21 (+0.09)	0.18 (+0.12)
MAE	–	–	0.64	0.55	0.49

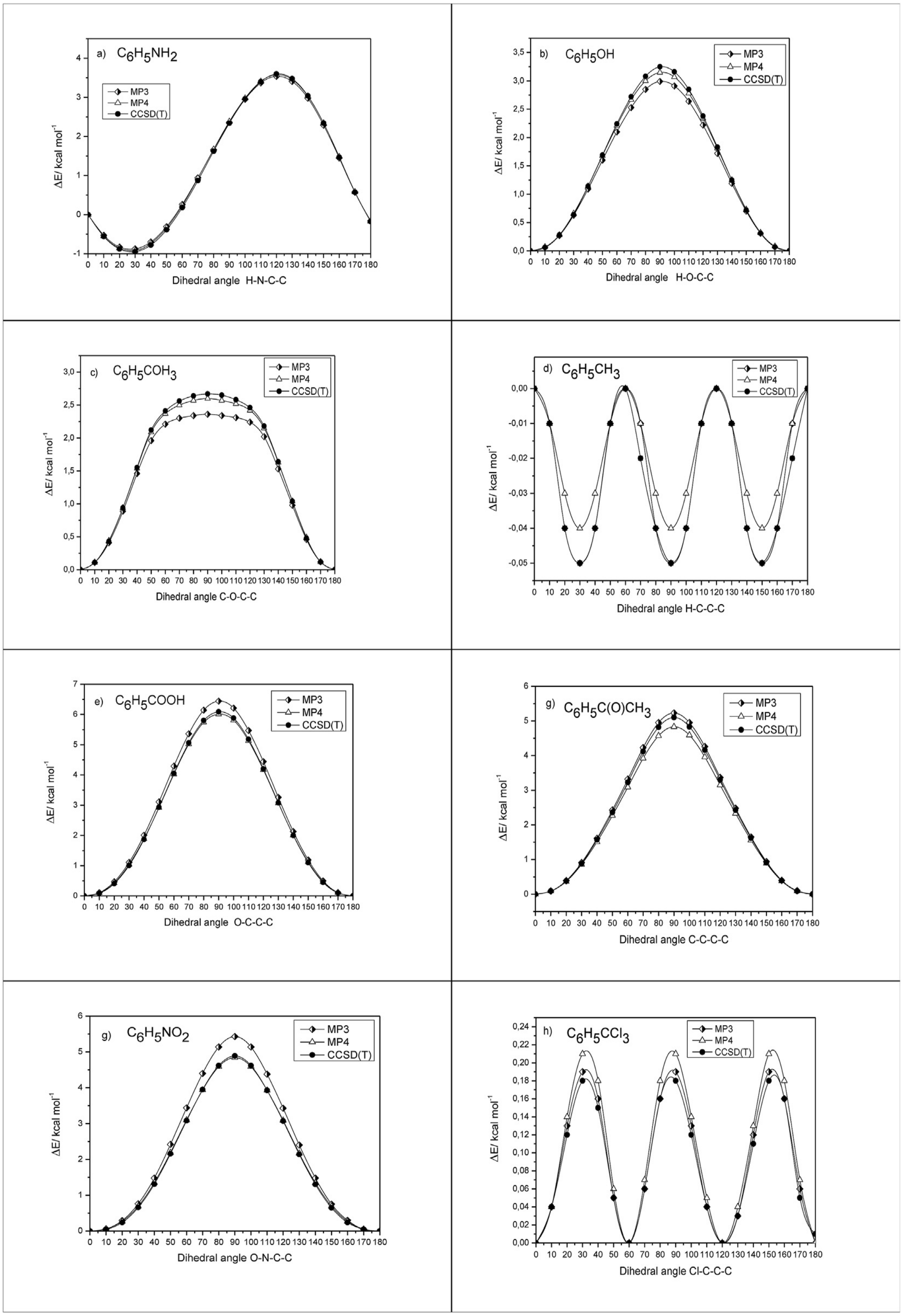

Figure 2. Relative energies calculated as a function of the dihedral angle for: a) Aminobenzene, b) Hydroxybenzene, c) Methoxybenzene, d) Methylbenzene, e) Nitrobenzene, f) Benzoic acid, g) Acetophenone and h) Trichloromethylbenzene.

electron withdrawing groups. The other systems are represented in the supplementary material, Tables S3 and S4.

Table 4 presents the NBO results of the internal rotation of methylbenzene at the minimum dihedral angle at 0° and maximum at 60°. The main interactions between the occupied bonding and unoccupied antibonding orbitals between the substituent and the aromatic ring show that the difference in energies found between the conformations is not significant. Interaction values are low <5.85 kcal mol^{-1} which justifies the free rotation of the rotor. The same trend can be seen for the trichloromethylbenzene molecule, Table S5.

Table 2. The donor-acceptor NBO interactions, second order perturbation energy ($\Delta E^{(2)}$), in kcal mol^{-1}, energy differences between orbitals (ε_i-ε_j), and Fock matrix elements (F (i,j)) in a.u. for the main interactions of the substituent group with the aromatic ring of hydroxybenzene.

NBO donor (i)	NBO receiver (j)	$\Delta E^{(2)}$	ε_i-ε_j	F (i,j)
Dihedral angle 0°				
σ C2 – C3	σ* C1 – O7	5.15	1.56	0.080
σ C5 – C6	σ* C1 – O7	4.39	1.55	0.074
σ O7 – H8	σ* C1 – C6	5.77	1.80	0.091
n σ O7	σ* C1 – C2	7.85	1.69	0.103
n π O7	π* C1 – C2	34.52	0.68	0.147
Dihedral angle 90°				
σ C2 – C3	σ* C1 – O7	4.84	1.53	0.077
σ C5 – C6	σ* C1 – O7	4.84	1.53	0.077
σ O7 – H8	π* C1 – C2	5.93	1.11	0.079
n σ O7	σ* C1 – C2	8.97	1.35	0.098
n σ O7	σ* C1 – C6	9.03	1.35	0.099
n π O7	π C1 – C2	7.04	1.03	0.083

In general, it can be inferred that when comparing the NBOs analysis, it is observed that the rotational barriers of the electron donor groups are lower than those of the electron withdrawing groups due to the interaction of the orbitals being less energetic. For the free rotors, there is no significant energy difference between the interactions of the NBO orbitals when the bond is twisted.

3.3. *Quantum Theory of Atoms in Molecules – QTAIM*

Table 4. The donor-acceptor NBO interactions, second order perturbation energy ($\Delta E^{(2)}$), in kcal mol^{-1}, energy differences between orbitals (ε_i-ε_j), and Fock matrix elements (F (i,j)) in a.u. for the main interactions of the substituent group with the aromatic ring of methylbenzene.

NBO donor (i)	NBO receptor (j)	$\Delta E^{(2)}$	ε_i-ε_j	F (i,j)
Dihedral angle 30°				
π C1 – C2	σ* C7 – H9	4.20	0.94	0.062
σ C2 – C3	σ* C1 – C7	4.16	1.60	0.073
σ C5 – C6	σ* C1 – C7	4.16	1.61	0.073
σ C7 – H8	σ* C1 – C6	4.74	1.53	0.076
σ C7 – H9	σ* C1 – C2	4.70	1.54	0.076
σ C7 – H10	π* C1 – C2	5.83	0.86	0.069
Dihedral angle 60°				
π C1 – C6	σ* C1 – H8	3.61	0.94	0.057
π C1 – C6	σ* C7 – H9	3.61	0.94	0.057
σ C2 – C3	σ* C1 – C7	4.10	1.61	0.073
σ C5 – C6	σ* C1 – C7	4.22	1.60	0.074
σ C7 – H8	π* C1 – C6	4.41	0.87	0.060
σ C7 – H9	σ* C1 – C2	5.58	1.53	0.083
σ C7 – H10	π* C1 – C6	4.41	0.87	0.060

For the QTAIM study the BCP properties were analyzed $\rho(r)$, $\nabla^2\rho(r)$ and $\varepsilon(r)$, around the bond C–Y, on what Y is the atom bonded to the aromatic ring of the substituent. The systems were divided into four classes of substituents: a) –OH and –OCH_3; b) –COOH and –$COCH_3$; c) –CH_3 and –CCl_3 and d) –NH_2 and –NO_2. The results for the QTAIM analysis are shown in Table 5 for the dihedrals angles at minimum and maximum.

For the class a) it is possible to observe that the C–O bond had a decrease in electronic density from the critical point of the bond in the 0° dihedral angle to the 90° dihedral angle. This difference is due to the fact that when the substituent is in the plane of the ring there is a greater electronic density due to the resonance of the substituent with the ring. Likewise, there is a significant increase in the ellipticity values ($\varepsilon(r)$) when the structure is at maximum energy showing a change in the symmetry of the bond. The values of the laplacian of the electronic density become more negative when the dihedral angle changes from 0° to 90°.

Table 3. The donor-acceptor NBO interactions, second order perturbation energy ($\Delta E^{(2)}$), in kcal mol^{-1}, energy differences between orbitals (ε_i-ε_j), and Fock matrix elements (F (i,j)) in a.u. for the main interactions of the substituent group with the aromatic ring of benzoic acid.

NBO donor (i)	NBO receptor (j)	$\Delta E^{(2)}$	ε_i-ε_j	F (i,j)
Dihedral angle 0°				
σ C2 – C3	σ* C1 – C7	3.68	1.62	0.070
σ C5 – C6	σ* C1 – C7	3.07	1.62	0.064
π C1 – C2	π* C7 – O8	29.07	0.51	0.114
π C7 – O8	π* C1 – C2	4.05	0.70	0.052
σ O9 – H10	σ* C1 – C7	4.91	1.67	0.082
n π O8	σ* C1 – C7	22.85	1.13	0.146
n π O8	σ* C7 – O9	45.43	1.05	0.197
n σ O9	σ* C7 – O8	8.12	1.80	0.108
n π O9	π* C7 – O8	60.03	0.71	0.187
π* C1 – C2	π* C7 – O8	125.06	0.03	0.101
Dihedral angle 90°				
σ C2 – C3	σ* C1 – C7	3.50	1.60	0.067
σ C5 – C6	σ* C1 – C7	3.50	1.60	0.067
π C1 – C6	σ* C7 – O8	4.58	1.23	0.073
π C1 – C6	σ* C7 – O9	6.03	0.93	0.071
σ O9 – H10	σ* C1 – C7	4.85	1.65	0.081
n π O8	σ* C1 – C7	22.76	1.12	0.145
n π O8	σ* C7 – O9	45.28	1.05	0.197
n σ O9	σ* C7 – O8	8.27	1.80	0.109
n π O9	π* C7 – O8	63.23	0.72	0.190
π*C1 – C6	σ* C7 – O9	3.35	0.43	0.073

Table 5. Topological parameter values for the bonds between the carbon atom of the aromatic ring and the atom of the substituent bonded to the ring in the dihedrals angles of minimum and maximum energy. Values in a.u.

Class	Molecule	Dihedral angle	Bond	$\rho(r)$	$\nabla^2\rho(r)$	$\varepsilon(r)$
a)	Hydroxybenzene	0°	C–O	0.290449	-0.491108	0.015771
		90°	C–O	0.281243	-0.600981	0.042263
	Methoxybenzene	0°	C–O	0.292703	-0.473578	0.033698
		90°	C–O	0.288563	-0.611756	0.042060
b)	Benzoic acid	0°	C–C	0.275681	-0.746648	0.108503
		90°	C–C	0.274805	-0.750669	0.031375
	Acetophenone	0°	C–C	0.268539	-0.690458	0.089886
		90°	C–C	0.268752	-0.700733	0.014751
c)	Methylbenzene	30°	C–C	0.256273	-0.631704	0.027424
		60°	C–C	0.256181	-0.631223	0.027100
	Trichloromethylbenzene	0°	C–C	0.260163	-0.645067	0.038089
		30°	C–C	0.259742	-0.642609	0.037930
d)	Aminobenzene	30°	C–N	0.302696	-1.003639	0.087892
		120°	C–N	0.283863	-0.847213	0.026734
	Nitrobenzene	0°	C–N	0.266460	-0.787131	0.115276
		90°	C–N	0.273264	-0.858096	0.057027

For rotors –COOH and $–COCH_3$ (class b) the results show that for the rotation over the C–C bonds there is little variation in the electronic density and also in the values of the laplacian of the electronic density when comparing the two conformations. The ellipticity value decays considerably from the 0° dihedral angle to the 90° dihedral angle showing the change in the symmetry of the chemical bond.

For free rotors ($–CH_3$ and $–CCl_3$, class c) the topological parameters show that the rotation over the C–C bonds had little change for all properties analyzed. Finally, for the class d) it is possible to infer that for the rotor $–NH_2$ the $\rho(r)$ and the $\nabla^2\rho(r)$ decrease when the structure changes the dihedral angle from 30° to 120° equal to the other electron donor groups of the class a), however the $\varepsilon(r)$ presented an opposite trend with a significant decrease in value when it changes from 30° to 120°. For the rotor $–NO_2$ there is a significant increase in the values of $\rho(r)$ and the $\nabla^2\rho(r)$ when the dihedral angle varies from 0° to 90° differently from the values found for benzoic acid and acetophenone. The exceptions of systems when compared to their classes can be explained by different symmetry of the rotors.

4. Conclusion

According to the results found, the methods used describe the systems adequately, because the MAEs were relatively low (<1 kcal mol^{-1}) and the CCSD(T) method presented the lowest MAE with a value of 0.49 kcal mol^{-1}.

The NBO analysis showed that, for the electron donating groups, which have lower rotational barrier values than the electron withdrawing groups, the values the interactions with second order perturbation energy $\Delta E^{(2)}$ between orbitals are less than for electron withdrawing groups. For structures with a free rotor, the energy values of the interactions between orbitals shows little significant change when rotation occurs.

The QTAIM analyses proved that the height of the rotational barriers for the donating groups is influenced by the loss of electronic density when the substituent is perpendicular to the plane of the aromatic ring. An increase in ellipticity is observed, which is due to the increase in the character π, given by the increase in the number of overlapping orbitals. For the electron withdrawing groups, the loss of electronic density is little influenced. Two structures showed free rotation, that is, methylbenzene and trichloromethylbenzene and did not show significant difference between the maximum and minimum conformations due to the topological properties studied. The aminobenzene and nitrobenzene presented exceptions when compared to their classes and can be explained by different symmetry of the rotors.

Declarations

Author contribution statement

Daniel Rodrigues Lima: Conceived and designed the experiments; Performed the experiments.

Sílvio Quintino de Aguiar Filho, Laura Beatriz Camargo do Oh, Anna Karla dos Santos Pereira: Analyzed and interpreted the data.

Douglas Henrique Pereira: Analyzed and interpreted the data; Wrote the paper.

Funding statement

This work was supported by CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Coordination of Improvement of Higher Education Personnel - Brazil), Funding Code 001 CAPES and the Brazilian Council of Technological and Scientific Development (CNPq, scholarship No. 164658/2018-1). Douglas Henrique Pereira was supported by the National Center for High Performance Processing (Centro Nacional de Processamento de Alto Desempenho – CENAPAD) in São Paulo, UNICAMP (Universidade de Campinas) and FAPESP (FAPESP - Fundação de Amparo à Pesquisa do Estado de São Paulo - Center for Computational Engineering and Sciences, Grant 2013/08293-7, and Grant 2017/11485-6), for computational resources.

Competing interest statement

The authors declare no conflict of interest.

Additional information

Supplementary content related to this article has been published online at https://doi.org/10.1016/j.heliyon.2020.e04957.

References

[1] T.W.G. Solomons, C.B. Fryhle, Organic Chemistry, ninth ed., John Wiley and Sons, Inc., New York, 2008.

[2] F.A. Carey, R.J. Sundberg, Advanced Organic Chemistry. Part A: Estructure and Mechanisms, fifth ed., Springer Science & Business Media, LLC, USA, 2007. University of Virginia.

[3] K.P.C. Vollhardt, N.E. Schore, Organic Chemistry: Structure and Function, fourth ed., Freeman and Company, New York, 2003.

[4] A. Domenicano, P. Murray-Rust, Geometrical substituent parameters for benzene derivatives: inductive and resonance effects, Tetrahedron Lett. 20 (1979) 2283–2286.

[5] D.H. Pereira, L.C. Ducati, R. Rittner, R. Custodio, A study of the rotational barriers for some organic compounds using the G3 and G3CEP theories, J. Mol. Model. 20 (2014) 2199.

[6] S.Q. de AguiarFilho, A.M.F. Costa, I.H.S. Ribeiro, R. Custodio, D.H. Pereira, Theoretical study of the internal rotational barriers of fluorine, chlorine, bromine, and iodine-substituted ethanes, Comput. Theor. Chem. 1166 (2019) 112589.

[7] A.E. Reed, F. Weinhold, Natural bond orbital analysis of internal rotation barriers and related phenomena, Isr. J. Chem. 31 (1991) 277–285.

[8] S. Liu, Origin and nature of bond rotation barriers: a unified view, J. Phys. Chem. 117 (2013) 962–965.

[9] X. Chang, P. Su, W. Wu, Internal rotation barrier of the XH 3 YH 3 (X, Y = C or Si) molecules. An energy decomposition analysis study, Chem. Phys. Lett. 610–611 (2014) 246–250.

[10] A. Ebrahimi, S.M. Habibi, A. Sanati, M. Mohammadi, A comparison of C–C rotational barrier in [2]staffane, [2]tetrahedrane and ethane, Chem. Phys. Lett. 466 (2008) 32–36.

[11] A.M.A. da Costa, L.A.E.B. de Carvalho, J.J.C. Teixeira-Dias, E.F.G. Barbosa, I.M.S. Lampreia, The temperature dependence of the Raman spectrum and gauche interactions of tri- N -butylamine: a conformational study, Can. J. Chem. 65 (1987) 384–390.

[12] J.J.C. Teixeira-Dias, L.A.E.B. de Carvalho, A.M.A. da Costa, I.M.S. Lampreia, E.F.G. Barbosa, Conformational studies by Raman spectroscopy and statistical analysis of gauche interactions in n-butylamine, Spectrochim. Acta Mol. Spectros 42 (1986) 589–597.

[13] Ş. Yurdakul, S. Tanrıbuyurdu, Theoretical and experimental study of solvent effects on the structure, vibrational spectra, and tautomerism of 3-amino-1,2,4-triazine, J. Mol. Struct. 1052 (2013) 57–66.

[14] S. Chakrabarty, B. Bagchi, Self-organization of n -alkane chains in water: length dependent crossover from helix and toroid to molten globule, J. Phys. Chem. B 113 (2009) 8446–8448.

[15] P.I. Nagy, G. Alagona, C. Ghio, K. Takács-Novák, Theoretical conformational analysis for neurotransmitters in the gas phase and in aqueous solution, Norepinephrine, J. Am. Chem. Soc. 125 (2003) 2770–2785.

[16] R.K. Sinha, Ab initio and NBO studies of methyl internal rotation in 1-methyl-2(1H)-quinolinone: effect of aromatic substitution to 1-methyl-2(1H)-pyridone, J. Mol. Model. 26 (2020) 92.

[17] R. Cimiraglia, H.-J. Hofmann, Rotation and inversion states in thermal E/Z isomerization of aromatic azo compounds, Chem. Phys. Lett. 217 (1994) 430–435.

[18] P.C. Chen, S.C. Chen, Theoretical study of the internal rotational barriers in nitrobenzene, 2-nitrotoluene, 2-nitrophenol, and 2-nitroaniline, Int. J. Quant. Chem. 83 (2001) 332–337.

[19] M. Staikova, I.G. Csizmadia, Ab initio investigation of internal rotation in conjugated molecules and the orientation of NO2 in nitroaromatics: nitrobenzene, o-monofluoro- and o,oH-difluoro-nitrobenzenes, J. Mol. Struct. (1999) 6.

[20] K.P.R. Nair, S. Herbers, J.-U. Grabow, A. Lesarri, Internal rotation in halogenated toluenes: rotational spectrum of 2,3-difluorotoluene, J. Mol. Spectrosc. 349 (2018) 37–42.

[21] E.D. Glendening, C.R. Landis, F. Weinhold, Natural bond orbital methods, WIREs Comput. Mol. Sci. 2 (2012) 1–42.

[22] R.F.W. Bader, H. Essén, The characterization of atomic interactions, J. Chem. Phys. 80 (1984) 1943–1960.

[23] R.F.W. Bader, Atoms in Molecules: A Quantum Theory, first ed., Oxford Univ. Press, Oxford, 1990.

[24] D. Ferro-Costas, A. Vila, R.A. Mosquera, Anomeric effect in halogenated methanols: a Quantum theory of atoms in molecules study, J. Phys. Chem. 117 (2013) 1641–1650.

[25] T.A. Keith, AIMAll (Version 17.11.14), TK Gristmill Software, Overland Park KS, USA, 2017. aim.tkgristmill.com.

[26] J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian09, Revision D.1, Gaussian, Inc., Wallingford, CT, 2009.

[27] G.E. Campagnaro, L. Wood, G.E. Campagnaro, J.L. Wood, The vibrational spectra and origin of torsional barriers in some aromatic systems, J. Mol. Struct. 6 (1970) 117–132 (1970).

[28] N.W. Larsen, Microwave spectra and internal rotation of 4-fluorophenol, 4-chlorophenol and 4-bromophenol, J. Mol. Struct. 144 (1986) 83–99.

[29] P.J. Breen, J.A. Warren, E.R. Bernstein, A study of nonrigid aromatic molecules by supersonic molecular jet spectroscopy. I. Toluene and the xylenes, J. Chem. Phys. 87 (1987) 1917.

[30] D.G. Lister, The barrier to internal rotation of the methoxy group in anisoles: evidence from the microwave spectrum of p-fluoroanisole, J. Mol. Struct. 68 (1980) 33–40.

[31] M. Onda, M. Asai, K. Takise, K. Kuwae, K. Hayami, A. Kuroe, M. Mori, H. Miyazaki, N. Suzuki, I. Yamaguchi, Microwave spectrum of benzoic acid, J. Mol. Struct. 482–483 (1999) 301–303.

[32] T. Drakenberg, J.M. Sommer, R. Jost, 13C nuclear magnetic resonance studies on acetophenones: barriers to internal rotation, Org. Magn. Reson. 8 (1976) 579–581.

[33] K.B. Borisenko, I. Hargittai, Barrier to internal rotation of the nitro group in ortho-nitrophenols from gas-phase electron diffraction, J. Mol. Struct. 382 (1996) 171–176.

[34] T. Matsuyoshi, K. Iijima, Internal rotation and barrier height of CCl3 group in trichloromethylbenzene as studied by gas-phase electron diffraction, J. Mol. Struct. 378 (1996) 199–203.