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

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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
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-phenyl diazene 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.

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, C₆H₅NH₂, C₆H₅OH, C₆H₅OCH₃, C₆H₅CH₃, C₆H₅NO₂, C₆H₅COOH, C₆H₅Cl(O)CH₃, and C₆H₅CCl₃ are shown in Table 1. The values for deviations from calculated C₆H₅OCH₃, C₆H₅CH₃, C₆H₅NO₂, C₆H₅COOH, C₆H₅Cl(O)CH₃, and C₆H₅NO₂ the rotational barrier pro

 equations and experimental values are shown in parentheses and were calculated by the difference between experimental and theoretical values, ΔE_{dev} = E_{exp} - 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).

\[
\text{MAE} = \left( \frac{\sum_{k=1}^{N} |x_{ik} - x_{jk}|}{N} \right)
\]

xₖ is the experimental value and xₖ 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 except for the withdrawing groups are greater in relation to the height of the aromatic ring, at 0°, there is a strong interaction between the bonding pi orbital (π*) with antibonding pi orbital (π) 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 NOB 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 NOB are greater than in 90°. The results also show that for the electron withdrawing group, the NBO found have high values of ΔE(2) mainly for interactions: π* C5 → C6 → π* C12 → O13, n π O14 → π* C12 → O13 and n π O13 → σ* C12 → O14. The values of the orbital interactions justify the greater rotational barriers of the

One can note that the potential energy surface of the C₆H₅CH₂ compound shows three equivalent minima at 30°, 90° and 150° and three equivalent maxima at 60°, 120° and 180°, whereas C₆H₅CCl₃ 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 (ΔE²) [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, methylenzene, 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 (ΔE(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) 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.

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 (2d, 2f, p) basis set. Data in kcal mol⁻¹.

| Molecules          | Exp. | Ref. | MP3     | MP4     | CCSD(T) |
|--------------------|------|------|---------|---------|---------|
| Electron donating groups |
| C₆H₅NH₂            | 3.50 | [27] | 4.43 (-0.93) | 4.51 (+0.02) | 4.55 (+0.05) |
| C₆H₅OH            | 3.47 | [28] | 2.98 (+0.49) | 3.15 (+0.32) | 3.24 (+0.23) |
| C₆H₅OCH₃          | 0.03 | [29] | 0.05 (-0.02) | 0.04 (+0.01) | 0.05 (+0.02) |
| C₆H₅CH₃           | 3.60 | [30] | 2.35 (+1.25) | 2.59 (+1.01) | 2.67 (+0.93) |
| Electron withdrawing groups |
| C₆H₅COOH          | 5.10 | [31] | 6.43 (-1.33) | 6.01 (-0.91) | 6.08 (-0.98) |
| C₆H₅Cl(O)CH₃      | 5.40 | [32] | 5.23 (+0.17) | 4.83 (+0.57) | 5.10 (+0.30) |
| C₆H₅NO₂           | 4.56 | [33] | 5.42 (-0.86) | 4.83 (0.27) | 4.88 (-0.32) |
| C₆H₅CCl₃         | 0.30 | [34] | 0.19 (+0.11) | 0.21 (+0.09) | 0.18 (+0.12) |
| MAE               | –    | –    | 0.64     | 0.55     | 0.49     |
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 $0^\circ$ and maximum at $60^\circ$. 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 $<5.85 \text{ kcal mol}^{-1}$ which justifies the free rotation of the rotor. The same trend can be seen for the trichloromethylbenzene molecule, Table S5.

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.
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

For the QTAIM study the BCP properties were analyzed $\rho(r)$, $\nabla^2 \rho(r)$ and $\epsilon(r)$, 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 ($\epsilon(r)$) 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 2. The donor-acceptor NBO interactions, second order perturbation energy ($\Delta\epsilon^{(2)}$), in kcal mol$^{-1}$, energy differences between orbitals ($\epsilon_i-\epsilon_j$), 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 receptor (j) | $\Delta\epsilon^{(2)}$ | $\epsilon_i-\epsilon_j$ | $F_{i,j}$ |
|--------------|------------------|------------------------|------------------------|-----------|
| 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 C7 – O8   | σ* C1 – C2       | 7.85                   | 1.69                   | 0.103     |
| n π O7      | π σ C1 – C2      | 34.52                  | 0.68                   | 0.147     |

### Table 3. The donor-acceptor NBO interactions, second order perturbation energy ($\Delta\epsilon^{(2)}$), in kcal mol$^{-1}$, energy differences between orbitals ($\epsilon_i-\epsilon_j$), 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) | $\Delta\epsilon^{(2)}$ | $\epsilon_i-\epsilon_j$ | $F_{i,j}$ |
|--------------|------------------|------------------------|------------------------|-----------|
| 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     |
| π 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 π O9     | π* C7 – O8       | 8.12                   | 1.80                   | 0.108     |
| n π O9     | π* C7 – O8       | 60.03                  | 0.71                   | 0.187     |
| π σ C1 – C2 | π σ C7 – O8      | 125.06                 | 0.03                   | 0.101     |

### Table 4. The donor-acceptor NBO interactions, second order perturbation energy ($\Delta\epsilon^{(2)}$), in kcal mol$^{-1}$, energy differences between orbitals ($\epsilon_i-\epsilon_j$), 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) | $\Delta\epsilon^{(2)}$ | $\epsilon_i-\epsilon_j$ | $F_{i,j}$ |
|--------------|------------------|------------------------|------------------------|-----------|
| σ 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 – O8   | σ* C1 – C6       | 4.74                   | 1.53                   | 0.076     |
| π C7 – H9   | π* C1 – C2       | 4.70                   | 1.54                   | 0.076     |
| π C7 – H10  | π* C1 – C2       | 5.83                   | 0.86                   | 0.069     |

### Table 5. The donor-acceptor NBO interactions, second order perturbation energy ($\Delta\epsilon^{(2)}$), in kcal mol$^{-1}$, energy differences between orbitals ($\epsilon_i-\epsilon_j$), and Fock matrix elements ($F_{i,j}$) in a.u. for the main interactions of the substituent group with the aromatic ring of nitrobenzene.

| NBO donor (i) | NBO receptor (j) | $\Delta\epsilon^{(2)}$ | $\epsilon_i-\epsilon_j$ | $F_{i,j}$ |
|--------------|------------------|------------------------|------------------------|-----------|
| σ 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 – O8   | σ* C1 – C6       | 4.74                   | 1.53                   | 0.076     |
| π C7 – H9   | π* C1 – C2       | 4.70                   | 1.54                   | 0.076     |
| π C7 – H10  | π* C1 – C2       | 5.83                   | 0.86                   | 0.069     |
For rotors \(-\text{COOH}\) and \(-\text{COCH}_3\) (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 (–\text{CH}_3 and –\text{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 –\text{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 \(\epsilon(r)\) presented an opposite trend with a significant decrease in value when it changes from 30° to 120°. For the rotor –\text{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 \(\pi\), 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.

Silvio 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.

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**Competing interest statement**

The authors declare no conflict of interest.

**Additional information**

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