Rotational barrier and electron-withdrawing substituent effects: Theoretical study of $\pi$-conjugation in para-substituted anilines

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Abstract: The rotational barrier RB around C–NH$_2$ bond between the minimum and maximum states of 84 electron-withdrawing groups at para-position in aniline were studied at the density functional B3LYP/6-31G** level. The rotational barrier was found to correlate strongly with shortening of the C–NH$_2$ bond, increase of flattening of NH$_2$ group, decrease in negative natural charge on amino nitrogen, increase in minimum ionization potential around lone pair of amino nitrogen, increase in maximum (positive) electrostatic potential on amino hydrogens, increase in NH$_2$ stretching frequencies, and increase in stabilization energy. The rotational barrier was also found to correlate well with empirical $pK_a$ and Hammett $\sigma$ constants. The rotational barrier is shown to be a reliable quantum mechanical approach to measure $\pi$-conjugation in para-substituted anilines. Based on RB a quantitative scale is constructed for the ability of electron-withdrawing substituents to resonate with aniline. A quinone-like structure has been proposed for stronger electron-withdrawing substituents where an extension of resonance stabilization requires the simultaneous presence of electron donor (NH$_2$) and electron-withdrawing groups.

Keywords: Rotational barrier; substituent effects; electron-withdrawing groups; para-substituted anilines.

1. Introduction

Empirical Hammett parameters are used to describe substituent effects in various aromatic systems. Several physical and chemical parameters such as $pK_a$, proton NMR shift, and linear free energy of substituted compounds have been reported to correlate with Hammett constants. However, despite successful applications of Hammett constants, these are not very successful for substituents that were not common or substituents that cause a shift in the position of transition state. To beat this challenge, researchers have introduced new parameters to modify Hammett constants. Moreover, quantum chemical methods like electrostatic and ionization potentials, substituted effect stabilization energy (SESE) charge substituent active region (cSAR), Aromaticity indices such as harmonic oscillator model of aromaticity (HOMA) and nucleus independent chemical shifts (NICS), are also used to describe substituent effect in $\pi$-conjugated systems especially when they show strong correlations with Hammett constants.

Resonance stabilization has been found to be significantly enhanced by the simultaneous presence of both electron-donating and accepting groups, especially at para positions. Theoretical studies of substituent effect are shown to be promising for practical applications like in organic dyes and photochromic compounds. Modifying $\pi$-spacers of organic dyes by electron-withdrawing groups resulted in the expansion of their absorption range and achieving high performance dye-sensitized solar cell devices. Fluorine substituent exhibited a strong acceleration of the rate of cis-trans isomerization of ortho-fluoroazobenzene compounds and they also affected the conjugate system of E isomer. This lead to an increase in light conversion rate in these photoswitches.

The internal rotational barriers can be linked to conjugation in substituted aromatic systems only in few cases. In some studies, the presence of $\pi$-electron acceptors at para-position in phenol has been found to increase the rotational barrier due to enhancement of electronic delocalization. The increase in rotational barrier relates to the strength of conjugation in substituted nitrotoluenes, nitrophenols, and nitroanilines, especially in para-positions. The nitro group in these compounds is coplanar with the phenyl ring due to conjugation and resonance effects. The barrier to internal rotation increased with the strength of electron-donating substituents in para-substituted acetophenones where these substituents led to an increase in the double bond character of the phenyl-acetyl bond.

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A similar conclusion has been reached with para-substituted benzaldehydes and p-methoxyacylbenzenes. The strength of electron-donating and accepting groups based on quantum mechanical methods have been established mostly with some common substituents as shown from the above examples. The main exception is the classification of substituents from very strong to weak electron-donating/withdrawing groups based on molecular electrostatic potential (MESP) analysis. The MESP analysis has also been successful in the study of electron donor-acceptor non-covalent complexes.

Hence, with the exception of electrostatic potential studies, there is no quantum mechanical method that could quantify the substituent effect with a large number of substituents. Therefore, it is strongly desired to quantify the effects of a large variety of substituents by correlating them with many empirical and computational parameters. These parameters are mandatory for measuring the extent of $\pi$-conjugation, which is the underlying reason for resonance stabilization of para-substituted conjugated systems.

Spurred on by the importance of correlating a large number of substituents with the stability profile of conjugated systems, the internal rotational barrier was adopted as a quantum mechanical approach to quantify the electron-withdrawing substituents effects in 84 para-substituted anilines. The rotational barrier was correlated with empirical Hammett $\sigma_p$ and $pK_a$ constants, as well with geometric, atomic, molecular, and spectroscopic properties that are affected by electron-withdrawing groups. The substituents are classified between strongly to very weakly electron-withdrawing groups based on RB and their correlation with geometric, atomic, spectroscopic, and molecular properties.

\[ I(r) = \sum_i p_i(r) |\epsilon_i| / \rho(r) \]

Where $\rho(r)$ is the orbital electron density, $|\epsilon_i|$ is absolute orbital energy, and $\rho(r)$ is the total electron density. The maximum electrostatic potential was also calculated only if it was on amino hydrogens of both minimum and maximum states. The minimum ionization and maximum electrostatic potentials were evaluated from QSAR model. The stabilization energy was calculated using the relationship

\[ E_{\text{stabilization}} = E(\text{benzene}–X) + E(\text{aniline}–X) – E(\text{aniline}–X) – E(\text{benzene}) \]

Where $X$ is the electron-withdrawing substituent, the large value of stabilization energy means higher stabilization energy due to the substituent effect.

Stabilization energy = $E(\text{benzene}–X) + E(\text{aniline}–X) – E(\text{aniline}–X) – E(\text{benzene})$

2. Method

The internal rotation potential energy curves were obtained by performing geometry optimization calculations at a set of HNCC dihedral angles ranging from 0 to 130° with an increment of 10°. Close to maximum state the increment was decreased to 1° and then to 0.1°. The minimum equilibrium states were optimized separately.

The internal rotational barrier RB around the C–N bond in aniline was considered between the minimum equilibrium state at a dihedral angle $\theta$ between 14.71° and 16.42° and the maximum state at a dihedral $\theta$ between 120.23° and 122.60°. Except for the dihedral angle $\theta$, all the independent structural parameters were optimized. The symbol $\varphi$ represents the out-of-plane angle between the NH$_2$ plane and the plane formed between the benzene carbons and the nitrogen atom. The minimum ionization potential $I(r)$ was calculated only if it was on lone pair of the amino nitrogen in both minimum and maximum states. The ionization potential is defined by eq. (1)

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electrostatic potentials cannot be located for ionic species in Spartan. The $pK_a$ values for N(CH$_3$)$_2^+$ and NH$_3^+$ are unreasonably higher than expected, while N$_2$ is significantly an outlier in all plots.

3. Results and Discussion

3.1. Substituent effect on parameters of para-substituted anilines

Tables 1 and 2 show values of HNCC dihedral angle $\theta$, C–NH$_2$ bond length R(C–NH$_2$), H–N–H angle $\Lambda$, out-of-plane angle $\phi$, natural charge on amino nitrogen $Q_n$, minimum ionization potential $IP$, and maximum electrostatic potential $E_{\text{max}}$ for minimum and maximum states of 84 para-substituted anilines respectively. The available experimental geometrical values are written in parenthesis in Table 1. Also, the calculated N–H distance of amino group in aniline (1.009 Å) is in good agreement with the reported experimental values (0.999–1.026 Å). Therefore, the calculated values either fall within the experimental limits or are reasonably close to them. The calculated ionization potential is around 3 eV higher than experimental values of aniline and few available para-substituted anilines (7.70–8.64 eV). However, the experimental $IP$ values were found to increase with the increasing power of electron-donating substituents which is similar to the trend in calculated $IP$ here.

C–NH$_2$ bond distances for all para-substituted anilines are smaller or equal to that of aniline (1.394 Å) except for NHCN and F. The C–NH$_2$ bond for C(CN)=C(CN)$_2$ substituent is 1.365 Å which is the shortest compared to that of aniline. The shorter length of this single bond indicates the increase of its double bond ($\pi$ component) character. The C–NH$_2$ bond distance in maximum states are very close to each other and larger than those in minimum states (Table 2) due to the lack of conjugation. The H–N–H angles in minimum states of para-substituted anilines are larger than that for aniline. In contrast, the out-of-plane angles $\phi$ are smaller except a few exceptions listed at the bottom of Table 1. The increase in H–N–H angle and the decrease of out-of-plane angles in minimum states compared to maximum states are indicative of changing the geometry of NH$_2$ group from pyramidal to planar. The H–N–H and out-of-plane angles $\phi$ in maximum states remained almost unaffected by substituents due to lack of conjugation in maximum states. Thus, NH$_2$ group in maximum states adopts a typical pyramidal geometry. The decrease in the negative natural charge on amino nitrogen in minimum states (Table 1) suggests a shift of electronic density from nitrogen. The values of natural charge on amino nitrogen in maximum states are almost constant and more negative than those in minimum states.

Table 3 shows that the values of rotational barrier RB and the difference in C–NH$_2$ bond length, H–N–H bond angle, out-of-plane angle $\phi$, natural charge on amino nitrogen, minimum ionization potential, and maximum electrostatic potential, fall between the minimum and maximum states of para-substituted anilines. The substituents are arranged in order of decreasing rotational barrier between the two states. Table 4 shows the empirical $pK_a$ values, symmetric and asymmetric NH$_2$ stretching frequencies for the minimum states, empirical $\sigma_p$ values, and the stabilization energy for the minimum states. Plots of parameters in Table 3 versus rotational barriers have been presented in Fig. 1. An observation of Fig. 1a reveals that change in C–NH$_2$ bond is strongly correlated with RB and, referring to Tables 1 and 2, this correlation is mainly due to changes in minimum states. Bond order was calculated and found to increase, from 1.24 to 1.33, with the increasing power of electron-withdrawing substituents in the minimum states. The bond order remains constant at 1.16 for all substituents in maximum states. The shortening of C–NH$_2$ bond length and increase of bond order with increasing RB implies that there is an increase in double bond character with increasing RB. It is worth mentioning here that as RB increases, the C–NH$_2$ bond length becomes closer and even shorter than that of formamide (1.376 Å) which is almost planar. The strong correlation between the changes in H–N–H and out-of-plane angles shows, respectively, in Figs 1b and 1c demonstrates that amino group becomes more open and planar with increasing rotational barrier. The sum of three angles around amino nitrogen atom in minimum state with C(CN)=C(CN)$_2$ substituent, which has the highest RB, is only 5.62° less than the completely planar geometrical structure. The corresponding sum in aniline differs by 18.41° from the planar structure. The increase in flattening of the pyramidal NH$_2$ with the increasing power of electron-withdrawing substituents has been verified experimentally for many para-substituted anilines. The increase in double-bond character and the opening of the H–N–H angle with RB indicate that the lone pair on amino nitrogen involves more in $\pi$-conjugation as RB increases.

It can be seen from Fig. 1d that change in natural charge on the amino nitrogen atom is correlated well with RB. This is attributed to the prominent decrease in a negative value of natural charge in minimum states, as shown in Tables 1 and 2. The decrease in negative value of natural charge with the increase in RB can be attributed to the involvement of lone pair on amino nitrogen in bonding with the adjacent carbon atom of the benzene ring. Natural charges have been shown to be superior to other forms of charges in the systems like the one under study here.

It is found that the lowest ionization potential in most of the compounds studied here is associated with the lone pair of amino nitrogen. This potential is expected to increase with the involvement of the lone pair in conjugation.
Table 1. Calculated geometrical, atomic, and molecular parameters for minimum (equilibrium) state of para-substituted anilines. Experimental values are in parenthesis.

| Substituent | $\theta$ (deg) | $R$(C-NH$_2$) (Å) | $A$(H-N-H) (deg) | $\phi$ (deg) | $Q_{a}(N)$ (e) | IP (eV) | $E_{S_{\text{max}}}$ (kcal/mol) |
|-------------|----------------|-------------------|------------------|-------------|---------------|--------|-------------------|
| C(CN)$_2$=C(CN)$_2$ | 14.71 | 1.365 | 116.02 | 23.03 | -0.836 | 11.97 | 65.92 |
| N$_{2}$=N(CN) | 15.65 | 1.368 | 115.68 | 25.00 | -0.839 | 11.66 | 62.88 |
| SO$_2$(CF$_3$)$_3$ | 17.89 | 1.371 | 115.12 | 28.00 | -0.845 | 11.47 | 58.51 |
| PF$_3$ | 17.71 | 1.371 | 115.10 | 28.26 | -0.846 | 11.36 | 63.79 |
| SO$_2$CN | 16.84 | 1.369 | 115.36 | 26.49 | -0.843 | 11.78 | 56.29 |
| BCl$_2$ | 18.45 | 1.373 | 114.87 | 29.49 | -0.846 | 11.29 | 58.32 |
| COCl | 18.50 | 1.373 | 114.85 | 29.44 | -0.846 | 11.41 | 57.60 |
| NO | 18.41 | 1.372 | 114.77 | 29.76 | -0.845 | 11.57 | 60.64 |
| SO$_2$CF$_3$ | 17.70 | 1.372 | 115.05 | 28.28 | -0.846 | 11.64 | 61.68 |
| SO$_2$Cl | 18.08 | 1.372 | 114.95 | 28.65 | -0.846 | 11.68 | 62.43 |
| N(O)$_2$=N(CN) | 18.89 | 1.372 | 114.84 | 29.21 | -0.844 | 11.68 | 57.48 |
| COCl$_3$ | 18.82 | 1.374 | 114.72 | 30.12 | -0.847 | 11.36 | 61.18 |
| C(NO$_2$)$_3$ | 18.32 | 1.372 | 114.80 | 29.53 | -0.846 | 11.59 | 60.75 |
| SO$_2$F | 18.65 | 1.373 | 114.80 | 29.43 | -0.847 | 11.55 | 59.58 |
| PSCl$_2$ | 18.38 | 1.373 | 114.75 | 29.73 | -0.847 | 11.55 | 59.86 |
| P(CN)$_2$ | 19.05 | 1.374 | 114.64 | 30.22 | -0.848 | 11.48 | 59.87 |
| SO$_2$CH$_2$F | 18.72 | 1.374 | 114.78 | 29.64 | -0.848 | 11.48 | 59.87 |
| N$_{2}$=NCF$_3$ | 18.98 | 1.375 | 114.58 | 30.63 | -0.847 | 11.32 | 57.06 |
| COF | 20.08 | 1.376 | 114.25 | 32.12 | -0.849 | 11.24 | 56.21 |
| POCI$_2$ | 19.27 | 1.374 | 114.62 | 30.33 | -0.848 | 11.45 | 59.41 |
| POF$_2$ | 19.63 | 1.375 | 114.49 | 30.95 | -0.849 | 11.37 | 58.43 |
| NO$_2$ | 19.42 | 1.375 (1.371) | 114.47 (113.6) | 31.01 | -0.848 | 11.39 | 58.60 |
| SF$_3$ | 19.77 | 1.375 | 114.44 | 31.29 | -0.849 | 11.33 | 56.88 |
| SCI | 20.40 | 1.377 | 114.12 | 32.62 | -0.850 | 11.22 | 55.75 |
| SiCl$_3$ | 20.34 | 1.378 | 114.08 | 32.75 | -0.852 | 11.22 | 55.75 |
| CHO | 20.79 | 1.379 | 113.89 | 33.62 | -0.852 | 11.07 | 53.85 |
| PCl$_2$ | 20.65 | 1.377 | 114.11 | 32.63 | -0.851 | 11.18 | 56.22 |
| SiBr$_3$ | 20.65 | 1.378 | 113.93 | 33.41 | -0.852 | 11.19 | 55.22 |
| GeCl$_3$ | 20.29 | 1.377 | 114.09 | 32.63 | -0.852 | 11.28 | 57.23 |
| BF$_2$ | 21.46 | 1.381 | 113.69 | 34.56 | -0.854 | 10.97 | 51.78 |
| P(CF$_3$)$_2$ | 20.97 | 1.378 | 113.94 | 33.41 | -0.852 | 11.37 | 58.43 |
| COOH | 21.76 | 1.381 (1.381) | 113.61 (114) | 34.86 | -0.855 | 10.94 | 54.01 |
| SiF$_3$ | 21.25 | 1.380 | 113.70 | 34.36 | -0.854 | 11.11 | 54.01 |
| CN | 21.01 | 1.379 (1.36) | 113.84 | 33.67 | -0.853 | 11.21 | 56.54 |
| PF$_2$ | 21.74 | 1.381 | 113.59 | 34.86 | -0.854 | 11.21 | 53.22 |
| SO$_2$CH$_3$ | 20.63 | 1.379 | 114.08 | 32.77 | -0.853 | 11.20 | 56.00 |
| COCH$_3$ | 22.20 | 1.382 | 113.45 | 35.44 | -0.855 | 10.91 | 51.63 |
| SF$_3$ | 21.28 | 1.380 | 113.69 | 34.29 | -0.854 | 11.19 | 55.96 |
| SO$_2$NH$_2$ | 21.59 | 1.381 | 113.69 | 34.38 | -0.855 | 11.07 | 52.61 |
| 5-tetrazoly1 | 21.90 | 1.382 | 113.42 | 35.31 | -0.855 | 10.97 | 50.32 |
| SiCl$_3$CH$_3$ | 21.81 | 1.382 | 113.47 | 35.28 | -0.856 | 10.97 | 50.32 |
| CO$_2$C$_2$H$_5$ | 22.22 | 1.383 | 113.37 | 35.85 | -0.856 | 10.83 | 50.23 |
| CO$_2$CH$_3$ | 22.51 | 1.383 | 113.32 | 35.99 | -0.856 | 10.84 | 50.30 |
| PO(OH)$_2$ | 22.02 | 1.382 | 113.51 | 35.19 | -0.856 | 10.90 | 50.30 |
| COC$_2$H$_5$ | 22.38 | 1.382 | 113.39 | 35.66 | -0.855 | 10.90 | 51.36 |

Table 1 shows that there is a slight general increase in ionization potential with the increasing power of electron-withdrawing groups in the minimum state but the correlation with the difference in this potential between the minimum and maximum states are clearly shown in Fig. 1e. The local surface ionization energy minima on lone pair of amino nitrogen has been reported to correlate with Hammet $\sigma_{p}^0$ constant and with $pK_a$ in some para-substituted anilines.
| Substituent     | $\theta$ (deg) | $R$(C-NH$_2$) (Å) | $\Lambda$(H-N-H) (deg) | $\varphi$ (deg) | $Q_a$(N) (e) | $IP$ (eV) | $E_{S\text{max}}$ (kcal/mol) |
|-----------------|----------------|------------------|------------------------|---------------|-------------|----------|------------------|
| SCN             | 21.09          | 1.380            | 113.77                 | 33.90         | -0.854      | 55.93    |                                |
| C≡CCF$_3$       | 21.90          | 1.382            | 113.50                 | 35.07         | -0.855      | 11.08    | 54.31            |
| SeCN            | 21.11          | 1.380            | 113.78                 | 33.92         | -0.854      | 55.46    |                                |
| SCF$_3$         | 22.15          | 1.383            | 113.36                 | 35.64         | -0.857      | 52.76    |                                |
| SiF$_2$CH$_3$   | 22.54          | 1.384            | 113.19                 | 36.45         | -0.858      | 10.83    | 50.62            |
| SCH$_2$         | 23.16          | 1.385            | 113.01                 | 36.92         | -0.859      | 51.71    |                                |
| CF$_3$          | 22.81          | 1.385            | 113.02                 | 36.91         | -0.858      | 10.92    | 51.77            |
| CH(CN)$_2$      | 22.38          | 1.383            | 113.28                 | 35.84         | -0.857      | 11.11    |                                |
| CH$_2$=NOCH$_3$ | 23.27          | 1.386            | 112.86                 | 37.66         | -0.859      | 10.71    | 48.45            |
| CHBr$_2$        | 22.50          | 1.385            | 113.06                 | 36.75         | -0.858      | 10.89    | 51.80            |
| COCC$_3$        | 22.20          | 1.382            | 113.52                 | 35.20         | -0.855      | 10.91    | 51.40            |
| CHCl$_2$        | 22.77          | 1.385            | 112.96                 | 37.09         | -0.859      | 10.88    | 51.53            |
| CaF$_3$         | 23.49          | 1.387            | 112.75                 | 37.95         | -0.860      | 10.80    | 50.18            |
| Br(OH)$_2$      | 23.50          | 1.388            | 112.64                 | 38.52         | -0.861      | 10.60    |                                |
| SiH$_3$         | 23.75          | 1.388            | 112.58                 | 38.65         | -0.861      | 10.66    | 47.64            |
| CHF$_2$         | 23.36          | 1.387            | 112.71                 | 38.07         | -0.861      | 10.77    | 49.59            |
| CCH             | 23.90          | 1.388            | 112.58                 | 38.57         | -0.861      | 10.61    | 48.38            |
| CH$_2$Cl        | 24.50          | 1.389            | 112.33                 | 39.38         | -0.862      | 10.69    | 48.23            |
| CH$_2$Br        | 24.48          | 1.389            | 112.41                 | 39.11         | -0.861      | 48.49    |                                |
| SH              | 23.99          | 1.388            | 112.50                 | 38.78         | -0.862      | 48.59    |                                |
| GeH$_3$         | 24.33          | 1.390            | 112.30                 | 39.63         | -0.863      | 10.58    | 46.68            |
| Si(CH$_3$)$_2$CaH$_5$ | 24.72      | 1.390            | 112.30                 | 39.72         | -0.864      | 10.49    | 44.86            |
| Si(C$_2$H$_5$)$_3$ | 24.63     | 1.391            | 112.22                 | 39.92         | -0.864      | 10.49    | 44.91            |
| SeCH=CH$_2$     | 23.53          | 1.388            | 112.64                 | 38.36         | -0.861      | 48.88    |                                |
| P(C$_2$H$_5$)$_2$ | 24.26       | 1.389            | 112.56                 | 38.77         | -0.862      | 47.19    |                                |
| I               | 24.25          | 1.389 (1.43$^a$) | 112.38                 | 39.16         | -0.862      | 49.78    |                                |
| SCH=CH$_2$      | 23.80          | 1.389            | 112.43                 | 39.02         | -0.862      | 48.65    |                                |
| 2-furyl         | 24.50          | 1.391            | 112.13                 | 40.16         | -0.864      | 10.52    | 45.97            |
| Br              | 24.55          | 1.390 (1.401$^a$) | 112.21                 | 39.67         | -0.863      | 10.73    | 49.42            |
| CH$_2$CN        | 24.11          | 1.391            | 112.13                 | 39.97         | -0.864      | 10.67    | 48.96            |
| Cl              | 24.79          | 1.391 (1.381$^{1,2}$,1.386$^b$) | 112.08            | 40.09         | -0.864      | 10.70    | 49.06            |
| CH$_2$OH        | 25.31          | 1.394            | 111.78                 | 41.30         | -0.866      | 10.45    |                                |
| H               | 25.42          | 1.394 (1.402$^a$,1.407$^b$) | 111.77 (111.15$^a$,111.18$^b$, 111.7$^b$) | 41.33 (38.46$^b$) | -0.867      | 10.39    | 43.78            |
| CH$_2$COCH$_3$  | 25.03          | 1.392            | 112.02                 | 40.45         | -0.865      | 10.55    | 46.75            |
| N=C=O           | 24.63          | 1.391            | 112.06                 | 40.11         | -0.864      | 10.69    | 49.32            |
| CH$_3$F         | 25.08          | 1.393            | 111.90                 | 40.81         | -0.865      | 10.49    | 45.79            |
| N$_3$           | 25.28          | 1.393            | 111.84                 | 40.87         | -0.865      | 10.63    | 48.42            |
| NH$_2$CN        | 25.67          | 1.396            | 111.40                 | 42.19         | -0.868      | 10.58    |                                |
| F               | 26.42          | 1.397            | 111.23 (111.87$^a$)    | 42.73 (42.73$^c$) | -0.869      | 10.46    | 45.97            |

$^a$Ref. 31, $^b$Ref. 32, $^c$Ref. 33, $^d$Ref. 34, $^e$Ref. 36, $^f$Ref. 37, $^g$Ref. 38, $^h$Ref. 39, $^i$Ref. 40, $^j$Ref. 41, $^k$Ref. 33, $^l$Ref. 42, $^m$Ref. 43, $^n$Ref. 44
Table 2. Calculated geometrical, atomic, and molecular parameters for maximum state of para-substituted anilines.

| Substituent | $\theta$ (deg) | $R$(C-NH$_2$) (Å) | $A$(H-N-H) (deg) | $\phi$ (deg) | $Q_{a}(N)$ (e) | $IP$ (eV) | $E^\text{S}_{\text{max}}$ (kcal/mol) |
|-------------|----------------|-------------------|------------------|--------------|----------------|----------|----------------------|
| C(CN)=C(CN)$_2$ | 120.6 | 1.432 | 106.72 | 54.44 | -0.929 | 10.69 | 50.02 |
| N=N=NCN | 121.1 | 1.433 | 106.53 | 54.85 | -0.930 | 10.61 | 47.73 |
| SO$_2$C(CF$_3$)$_3$ | 121.2 | 1.433 | 106.69 | 54.67 | -0.929 | 10.47 | 45.64 |
| PF$_4$ | 120.7 | 1.434 | 106.30 | 55.34 | -0.929 | 10.72 | 40.43 |
| SO$_2$CN | 121.0 | 1.432 | 106.79 | 54.39 | -0.929 | 10.31 | 43.04 |
| BCl$_2$ | 121.6 | 1.435 | 106.34 | 55.35 | -0.929 | 10.44 | 45.54 |
| COCl | 121.5 | 1.434 | 106.55 | 54.90 | -0.929 | 10.30 | 44.51 |
| NO | 121.3 | 1.435 | 106.57 | 54.86 | -0.930 | 10.58 | 48.20 |
| SO$_2$CF$_3$ | 121.2 | 1.433 | 106.69 | 54.58 | -0.929 | 10.62 | 48.76 |
| SO$_2$Cl | 121.1 | 1.433 | 106.78 | 54.45 | -0.929 | 10.66 | 49.48 |
| N(O)=NCN | 122.09 | 1.432 | 106.86 | 54.21 | -0.928 | 10.39 | 44.71 |
| COCF$_3$ | 121.4 | 1.434 | 106.40 | 55.12 | -0.929 | 10.64 | 48.72 |
| C(NO$_2$)$_3$ | 121.3 | 1.432 | 106.74 | 54.51 | -0.928 | 10.39 | 47.57 |
| SO$_2$F | 121.3 | 1.433 | 106.62 | 54.71 | -0.929 | 10.61 | 48.49 |
| PCl$_2$ | 121.2 | 1.433 | 106.66 | 54.68 | -0.929 | 10.49 | 46.73 |
| NO$_2$ | 121.0 | 1.433 | 106.77 | 54.46 | -0.929 | 10.48 | 46.39 |
| SF$_3$ | 121.47 | 1.434 | 106.61 | 54.84 | -0.929 | 10.41 | 45.05 |
| SCI | 121.4 | 1.435 | 106.47 | 54.98 | -0.929 | 10.36 | 44.15 |
| SiCl$_3$ | 121.3 | 1.435 | 106.58 | 54.86 | -0.929 | 10.35 | 44.03 |
| CHO | 121.4 | 1.436 | 106.51 | 54.96 | -0.929 | 10.24 | 42.27 |
| PCl$_2$ | 121.2 | 1.434 | 106.56 | 54.87 | -0.929 | 10.49 | 43.92 |
| SiBr$_3$ | 121.4 | 1.435 | 106.46 | 55.03 | -0.929 | 10.32 | 43.46 |
| GeCl$_3$ | 121.2 | 1.434 | 106.63 | 54.69 | -0.929 | 10.44 | 45.52 |
| BF$_2$ | 121.3 | 1.436 | 106.27 | 55.44 | -0.929 | 10.16 | 40.71 |
| P(CF$_3$)$_2$ | 121.37 | 1.435 | 106.58 | 54.87 | -0.929 | 10.48 | 43.66 |
| COOH | 121.6 | 1.436 | 106.39 | 55.20 | -0.929 | 10.15 | 43.86 |
| SiF$_4$ | 121.4 | 1.435 | 106.53 | 54.95 | -0.929 | 10.32 | 43.05 |
| CN | 121.9 | 1.434 | 106.36 | 55.03 | -0.928 | 10.42 | 45.31 |
| PF$_3$ | 121.54 | 1.436 | 106.57 | 54.88 | -0.929 | 10.22 | 42.23 |
| SO$_2$CH$_3$ | 121.8 | 1.435 | 106.63 | 54.71 | -0.929 | 10.38 | 44.97 |
| COCH$_3$ | 121.6 | 1.436 | 106.43 | 55.08 | -0.929 | 10.14 | 40.67 |
| SF$_3$ | 121.48 | 1.434 | 106.72 | 54.58 | -0.928 | 10.43 | 45.06 |
| SO$_2$NH$_2$ | 121.4 | 1.435 | 106.64 | 54.75 | -0.929 | 10.29 | 46.39 |
| 5-tetrazolyl | 121.5 | 1.435 | 106.71 | 54.46 | -0.928 | 10.22 | 41.39 |
| SiCH$_2$CH$_3$ | 121.5 | 1.436 | 106.37 | 55.23 | -0.929 | 10.09 | 39.27 |
| CO$_2$CH$_3$ | 121.5 | 1.436 | 106.40 | 55.22 | -0.929 | 10.10 | 39.29 |
| CO$_2$H | 121.4 | 1.437 | 106.32 | 55.38 | -0.929 | 10.18 | 39.95 |
| PO(OH)$_2$ | 121.32 | 1.436 | 106.46 | 55.14 | -0.929 | 10.15 | 45.06 |
| CO$_2$H$_2$ | 121.98 | 1.436 | 106.19 | 55.54 | -0.929 | 10.31 | 43.11 |
Table 2. (continued)

| Substituent | $\theta$ (deg) | $R$(C-NH$_2$) (Å) | $\Lambda$(H-N-H) (deg) | $\varphi$ (deg) | $Q_0$(N) (e) | $IP$ (eV) | $E_{S\text{max}}$ (kcal/mol) |
|-------------|----------------|-------------------|-------------------|----------------|-------------|---------|-----------------------------|
| SeCN        | 121.18         | 1.435             | 106.50            | 54.89          | -0.928      | 44.67   |                             |
| SCF$_3$     | 121.25         | 1.435             | 106.56            | 54.89          | -0.929      | 42.24   |                             |
| SiF$_2$CH$_3$ | 121.1       | 1.437             | 106.39            | 55.23          | -0.929      | 10.12   | 40.03                        |
| SCHF$_2$    | 122.16         | 1.436             | 106.45            | 54.98          | -0.928      | 41.55   |                             |
| CF$_3$      | 121.3          | 1.436             | 106.54            | 54.86          | -0.928      | 10.24   | 41.74                        |
| CH(CN)$_2$  | 121.78         | 1.435             | 106.44            | 54.89          | -0.928      | 10.43   |                             |
| CH=NOCH$_3$ | 121.77         | 1.437             | 106.33            | 55.25          | -0.928      | 9.99    | 37.88                        |
| CHBr$_2$    | 121.4          | 1.436             | 106.57            | 54.83          | -0.928      | 10.17   | 41.18                        |
| COCsH$_6$   | 122.0          | 1.436             | 106.27            | 55.36          | -0.929      | 10.12   | 39.88                        |
| CHCl$_2$    | 120.87         | 1.436             | 106.31            | 55.21          | -0.928      | 10.21   | 41.11                        |
| CoF$_3$     | 121.5          | 1.436             | 106.45            | 55.03          | -0.928      | 10.13   | 40.08                        |
| B(OH)$_2$   | 121.8          | 1.438             | 106.31            | 55.45          | -0.929      | 9.95    |                             |
| SiH$_3$     | 121.7          | 1.437             | 106.42            | 55.17          | -0.929      | 10.01   | 37.98                        |
| CHF$_2$     | 121.36         | 1.436             | 106.47            | 55.00          | -0.928      | 10.15   | 39.98                        |
| CCH          | 121.4          | 1.437             | 106.47            | 54.97          | -0.928      | 10.04   | 38.47                        |
| CH$_2$Cl     | 122.3          | 1.437             | 106.40            | 55.06          | -0.928      | 10.06   | 39.14                        |
| CH$_2$Br     | 121.0          | 1.437             | 106.47            | 55.01          | -0.928      | 39.03   |                             |
| SH           | 121.4          | 1.437             | 106.44            | 55.02          | -0.928      | 39.40   |                             |
| GeH$_3$     | 121.4          | 1.437             | 106.41            | 55.15          | -0.928      | 9.97    | 37.37                        |
| Si(CH$_3$)$_2$CS$_2$ | 122.02 | 1.438 | 106.19 | 55.56 | -0.929 | 9.86 | 35.24 |
| Si(C$_3$H$_3$)$_3$ | 121.73 | 1.438 | 106.19 | 55.53 | -0.928 | 9.88 | 35.58 |
| SeCH=CH$_2$ | 121.23         | 1.437             | 106.20            | 55.30          | -0.927      | 38.31   |                             |
| P(C$_3$H$_2$)$_2$ | 122.6     | 1.438             | 106.13            | 55.59          | -0.928      | 37.04   |                             |
| I            | 122.1          | 1.436             | 106.43            | 54.93          | -0.927      | 40.08   |                             |
| SCH=CH$_2$  | 121.0          | 1.437             | 106.60            | 54.70          | -0.928      | 38.11   |                             |
| 2-furyl      | 121.7          | 1.437             | 106.40            | 55.05          | -0.928      | 9.90    | 36.28                        |
| Br           | 121.9          | 1.436             | 106.41            | 54.92          | -0.927      | 10.15   | 40.31                        |
| CH$_3$CN     | 121.1          | 1.437             | 106.44            | 54.98          | -0.928      | 10.10   | 39.45                        |
| Cl           | 121.9          | 1.436             | 106.40            | 54.90          | -0.927      | 10.13   | 39.98                        |
| CH$_2$OH     | 121.01         | 1.438             | 106.11            | 55.41          | -0.927      | 9.92    |                             |
| H            | 121.7          | 1.438             | 106.46            | 55.06          | -0.928      | 8.96    | 35.49                        |
| CH$_2$COCH$_3$ | 122.2        | 1.437             | 106.32            | 55.17          | -0.928      | 9.99    | 37.55                        |
| N=O=O       | 120.23         | 1.436             | 106.25            | 55.01          | -0.927      | 10.13   | 40.07                        |
| CH$_3$F      | 121.28         | 1.437             | 106.52            | 54.80          | -0.928      | 9.92    | 36.70                        |
| N$_3$        | 121.18         | 1.436             | 106.74            | 54.29          | -0.928      | 10.08   | 39.21                        |
| NHCN         | 121.17         | 1.436             | 106.56            | 54.43          | -0.926      | 10.10   |                             |
| F            | 121.12         | 1.437             | 106.43            | 54.73          | -0.927      | 10.02   | 37.99                        |
Table 3. Rotational barrier and differences of geometrical, atomic, and molecular parameters between minimum (Table 1) and maximum states (Table 2) of para-substituted anilines.

| Substituent     | RB  | $\Delta R$(C-NH$_2$) | $\Delta A$(H-N-H) | $\Delta \phi$ | $\Delta Q_a$(N) | $\Delta IP$ | $\Delta E_{\text{max}}$ |
|-----------------|-----|----------------------|-------------------|-------------|----------------|----------|----------------------|
| C(CN) = C(CN)$_2$ | 8.99 | -0.067               | 9.30              | -31.41      | 0.093          | 1.28     | 15.90               |
| N=NCN           | 8.75 | -0.065               | 9.15              | -29.85      | 0.091          |          | 15.15               |
| SO$_2$C(CF$_3$)$_3$ | 8.75 | -0.062               | 8.43              | -26.67      | 0.084          | 1.05     | 13.17               |
| PF$_4$          | 8.57 | -0.063               | 8.80              | -27.08      | 0.083          | 1.00     | 12.87               |
| SO$_2$CN        | 8.46 | -0.063               | 8.57              | -27.90      | 0.086          | 1.06     | 13.36               |
| BCl$_2$         | 8.22 | -0.062               | 8.53              | -25.86      | 0.083          | 0.98     | 14.94               |
| COCl            | 8.08 | -0.061               | 8.30              | -25.46      | 0.083          | 0.97     | 13.24               |
| NO              | 8.07 | -0.062               | 8.20              | -25.10      | 0.085          |          | 12.77               |
| SO$_2$CF$_3$     | 8.05 | -0.061               | 8.36              | -26.30      | 0.083          | 0.99     | 13.08               |
| SO$_2$Cl        | 8.04 | -0.061               | 8.17              | -25.80      | 0.083          | 1.02     | 12.44               |
| N(O)=NCN        | 8.00 | -0.060               | 7.98              | -25.00      | 0.084          | 1.02     | 12.92               |
| COCF$_3$        | 8.00 | -0.060               | 8.32              | -25.00      | 0.082          | 0.97     | 12.95               |
| C(NO$_2$)$_3$    | 7.93 | -0.060               | 8.06              | -24.98      | 0.082          | 0.95     | 12.77               |
| SO$_2$F         | 7.91 | -0.060               | 8.18              | -25.28      | 0.082          | 0.94     | 12.46               |
| PSCl$_2$        | 7.83 | -0.060               | 8.09              | -24.95      | 0.082          |          | 12.26               |
| P(CN)$_2$       | 7.81 | -0.059               | 7.87              | -24.24      | 0.081          |          | 12.85               |
| SO$_2$CHF$_2$   | 7.75 | -0.060               | 8.25              | -25.16      | 0.081          | 0.92     | 12.29               |
| N=NCF$_3$       | 7.72 | -0.060               | 8.11              | -24.35      | 0.082          | 0.96     | 12.33               |
| COF             | 7.71 | -0.059               | 7.85              | -23.01      | 0.080          | 0.87     | 12.91               |
| POCl$_2$        | 7.71 | -0.060               | 7.94              | -24.31      | 0.082          | 0.92     | 11.79               |
| POF$_2$         | 7.66 | -0.059               | 7.91              | -23.91      | 0.080          | 0.88     | 12.74               |
| NO$_2$          | 7.65 | -0.059               | 7.81              | -23.64      | 0.081          | 0.91     | 12.25               |
| SF$_3$          | 7.58 | -0.059               | 7.83              | -23.55      | 0.080          | 0.92     | 12.20               |
| SCI             | 7.44 | -0.058               | 7.66              | -22.49      | 0.079          |          | 11.83               |
| SiCl$_3$        | 7.32 | -0.057               | 7.50              | -22.11      | 0.077          | 0.87     | 12.03               |
| CHO             | 7.29 | -0.057               | 7.38              | -21.34      | 0.077          | 0.83     | 10.75               |
| PCl$_2$         | 7.28 | -0.057               | 7.55              | -22.24      | 0.078          |          | 11.71               |
| SiBr$_3$        | 7.26 | -0.057               | 7.47              | -21.62      | 0.077          | 0.86     | 11.58               |
| GeCl$_3$        | 7.22 | -0.057               | 7.46              | -22.06      | 0.077          | 0.84     | 12.30               |
| BF$_3$          | 7.22 | -0.055               | 7.42              | -20.88      | 0.075          | 0.81     | 11.77               |
| P(CF$_3$)$_2$   | 7.18 | -0.057               | 7.36              | -21.46      | 0.077          |          | 11.71               |
| COOH            | 7.08 | -0.055               | 7.22              | -20.34      | 0.074          | 0.79     | 11.07               |
| SiF$_4$         | 7.08 | -0.055               | 7.17              | -20.59      | 0.075          | 0.79     | 11.33               |
| CN              | 7.03 | -0.055               | 7.48              | -21.36      | 0.075          | 0.79     |                    |
| PF$_2$          | 6.99 | -0.055               | 7.02              | -20.02      | 0.075          |          | 10.96               |
| SO$_2$CH$_3$    | 6.97 | -0.056               | 7.45              | -21.94      | 0.076          | 0.82     | 11.22               |
| COCH$_3$        | 6.94 | -0.054               | 7.02              | -19.64      | 0.074          | 0.77     | 10.98               |
| SF$_3$          | 6.91 | -0.054               | 6.97              | -20.29      | 0.074          | 0.76     | 11.03               |
| SO$_2$NH$_2$    | 6.81 | -0.054               | 7.05              | -20.37      | 0.074          | 0.78     | 10.95               |
| 5-tetrazolyl     | 6.79 | -0.053               | 6.71              | -19.15      | 0.073          |          | 10.90               |
| SiH$_2$CH$_3$   | 6.78 | -0.054               | 7.10              | -19.95      | 0.073          | 0.75     |                    |
| CO$_2$C$_2$H$_5$| 6.78 | -0.053               | 6.97              | -19.37      | 0.073          | 0.74     |                    |
| CO$_2$H$_3$     | 6.76 | -0.054               | 7.00              | -19.39      | 0.073          | 0.74     |                    |
| PO(OM)$_2$      | 6.73 | -0.054               | 7.05              | -19.95      | 0.073          | 0.72     | 10.96               |
| COC$_2$H$_5$    | 6.72 | -0.054               | 7.20              | -19.88      | 0.074          | 0.75     | 11.01               |
| SCN             | 6.71 | -0.055               | 7.17              | -20.81      | 0.074          |          |                    |
| C=C CCF$_3$     | 6.70 | -0.053               | 7.05              | -19.87      | 0.073          | 0.77     | 11.41               |
| Substituent          | RB (kcal/mol) | $\Delta R$(C-NH$_2$) (Å) | $\Delta A$(H-N-H) (deg) | $\Delta \phi$ (deg) | $\Delta Q_e$(N) (e) | $\Delta IP$ (eV) | $\Delta E_{max}$ (kcal/mol) |
|----------------------|---------------|--------------------------|-------------------------|---------------------|---------------------|------------------|-----------------------------|
| SeCN                 | 6.69          | -0.055                   | 7.28                    | -20.97              | 0.074               | 10.87            |                             |
|                      |               |                          |                         |                     |                     |                  |                             |
| Table 3. (continued) |               |                          |                         |                     |                     |                  |                             |
| SCF$_3$              | 6.49          | -0.052                   | 6.80                    | -19.25              | 0.072               | 11.88            |                             |
| SiF$_2$CH$_3$        | 6.39          | -0.053                   | 6.80                    | -18.78              | 0.071               | 0.71             | 11.20                       |
| SCH$_2$F$_3$         | 6.36          | -0.051                   | 6.56                    | -18.06              | 0.069               | 10.79            |                             |
| CF$_3$               | 6.34          | -0.051                   | 6.48                    | -17.95              | 0.070               | 0.68             | 10.09                       |
| CH(CN)$_2$           | 6.29          | -0.052                   | 6.84                    | -19.05              | 0.071               | 0.68             | 10.52                       |
| CH$_3$NOCH$_3$       | 6.28          | -0.051                   | 6.53                    | -17.59              | 0.069               | 0.72             | 10.59                       |
| CHBr$_2$             | 6.27          | -0.051                   | 6.49                    | -18.08              | 0.070               | 0.72             | 10.16                       |
| COC$_2$H$_4$         | 6.14          | -0.054                   | 7.25                    | -20.16              | 0.074               | 0.79             | 10.02                       |
| CHCl$_3$             | 6.08          | -0.051                   | 6.65                    | -18.12              | 0.069               | 0.67             | 11.50                       |
| C$_2$F$_3$           | 6.06          | -0.049                   | 6.30                    | -17.88              | 0.068               | 0.67             |                             |
| B(OH)$_2$            | 6.06          | -0.050                   | 6.33                    | -16.93              | 0.068               | 0.65             | 10.57                       |
| SiH$_3$              | 5.95          | -0.049                   | 6.16                    | -16.52              | 0.068               | 0.65             | 10.62                       |
| CHF$_2$              | 5.93          | -0.049                   | 6.24                    | -16.93              | 0.067               | 0.62             | 11.52                       |
| CCH                  | 5.89          | -0.049                   | 6.11                    | -16.40              | 0.067               | 0.57             | 9.97                        |
| CH$_2$Cl             | 5.78          | -0.048                   | 5.93                    | -15.68              | 0.066               | 0.63             | 10.43                       |
| CH$_3$Br             | 5.77          | -0.048                   | 5.94                    | -15.90              | 0.067               | 0.67             | 10.10                       |
| SH                   | 5.69          | -0.049                   | 6.06                    | -16.24              | 0.066               |                  |                             |
| GeH$_3$              | 5.64          | -0.047                   | 5.89                    | -15.52              | 0.065               | 0.61             | 9.67                        |
| Si(CH$_3$)$_2$C$_6$H$_5$ | 5.64       | -0.048                   | 6.11                    | -15.84              | 0.065               | 0.63             | 9.77                        |
| Si(C$_2$H$_5$)$_3$   | 5.64          | -0.047                   | 6.03                    | -15.61              | 0.064               | 0.61             | 9.61                        |
| SeCH=CH$_2$          | 5.62          | -0.049                   | 6.44                    | -16.94              | 0.066               |                  | 10.02                       |
| Pt(C$_2$H$_5$)$_2$   | 5.57          | -0.049                   | 6.43                    | -16.82              | 0.066               |                  | 9.62                        |
| I                    | 5.52          | -0.047                   | 5.95                    | -15.77              | 0.065               |                  | 9.91                        |
| SCH=CH$_2$           | 5.44          | -0.048                   | 5.83                    | -15.68              | 0.066               |                  | 9.09                        |
| 2-furyl              | 5.40          | -0.046                   | 5.73                    | -14.89              | 0.064               | 0.62             | 9.46                        |
| Br                   | 5.32          | -0.046                   | 5.80                    | -15.25              | 0.064               | 0.58             | 10.63                       |
| CH$_2$CN             | 5.30          | -0.046                   | 5.69                    | -15.01              | 0.064               | 0.57             | 10.77                       |
| Cl                   | 5.16          | -0.045                   | 5.68                    | -14.81              | 0.063               | 0.57             | 9.19                        |
| CH$_2$OH             | 5.13          | -0.044                   | 5.67                    | -14.11              | 0.061               | 0.53             | 9.31                        |
| H                    | 5.12          | -0.044                   | 5.31                    | -13.73              | 0.061               | 0.53             | 9.62                        |
| CH$_3$COCH$_3$       | 5.11          | -0.045                   | 5.70                    | -14.72              | 0.063               | 0.56             | 9.33                        |
| N=C=O                | 5.02          | -0.045                   | 5.81                    | -14.90              | 0.063               | 0.56             | 10.56                       |
| CH$_3$F              | 5.01          | -0.044                   | 5.38                    | -13.99              | 0.063               | 0.57             | 10.87                       |
| N$_3$                | 4.80          | -0.043                   | 5.10                    | -13.42              | 0.063               | 0.55             | 10.15                       |
| NH$_2$CN             | 4.43          | -0.040                   | 4.84                    | -12.24              | 0.058               | 0.48             | 9.70                        |
| F                    | 4.18          | -0.040                   | 4.80                    | -12.00              | 0.058               | 0.44             | 10.53                       |
Table 4. Rotational barrier, empirical pKₐ constants, symmetric and asymmetric NH₂ stretching frequencies, empirical Hammett σᵣ constants, and the stabilization energy of para-substituted anilines.

| Substituent     | RB  | pKₐ | νₐ(NH₂) | νₐ(NH₂) | σᵣ | SE  |
|-----------------|-----|-----|---------|---------|-----|-----|
|                 | (kcal/mol) |     | (cm⁻¹)  | (cm⁻¹)  |     | (kcal/mol) |
| C(CN)=C(CN)₂    | 8.99 | 3669 | 3795    | 0.98    | 4.39 |
| N=NCN           | 8.75 | 3666 | 3790    | 1.03    | 4.19 |
| SO₂C(CF₃)₃     | 8.75 | 3660 | 3783    | 1.13    | 3.69 |
| PF₄             | 8.57 | 3664 | 3786    | 0.8     | 3.89 |
| SO₂CN           | 8.46 | 3667 | 3790    | 1.26    | 3.85 |
| BC₁₂            | 8.22 | 3660 | 3782    |         | 3.72 |
| COCI            | 8.08 | 3661 | 3782    | 0.61    | 3.47 |
| NO              | 8.07 | 3657 | 3778    | 0.91    | 3.42 |
| SO₂CF₃         | 8.05 | 3657 | 3781    | 0.96    | 3.39 |
| SO₂Cl           | 8.04 | 3663 | 3785    | 1.11    | 3.33 |
| N(O)=NCN        | 8.00 | 3662 | 3784    | 0.89    | 3.28 |
| COCF₃           | 8.00 | 3660 | 3781    | 0.8     | 3.39 |
| C(NO₂)₃        | 7.93 | 3661 | 3783    | 0.82    | 3.37 |
| SO₂F            | 7.91 | 3662 | 3783    | 0.91    | 3.24 |
| PSCl₂           | 7.83 | 3660 | 3782    | 0.8     | 3.20 |
| P(CN)₂          | 7.81 | 3657 | 3777    | 0.9     | 3.02 |
| SO₂CHF₂         | 7.75 | 3656 | 3778    | 0.86    | 2.97 |
| N=NCF₃          | 7.72 | 3657 | 3777    | 0.68    | 3.01 |
| COF             | 7.71 | 3655 | 3774    | 0.7     | 2.96 |
| POCl₂           | 7.71 | 3656 | 3776    | 0.9     | 3.14 |
| POF₂            | 7.66 | 3658 | 3778    | 0.89    | 3.06 |
| NO₂             | 7.65 | 3659 | 3779    | 0.778   | 2.84 |
| SF₃             | 7.58 | 3656 | 3776    | 0.8     | 3.05 |
| SCl             | 7.44 | 3651 | 3769    | 0.48    | 2.70 |
| SiCl₃           | 7.32 | 3654 | 3772    | 0.56    | 2.66 |
| CHO             | 7.29 | 3646 | 3765    | 0.42    | 2.49 |
| PCl₂            | 7.28 | 3655 | 3774    | 0.61    | 2.61 |
| SiBr₃           | 7.26 | 3652 | 3771    | 0.57    | 2.58 |
| GeCl₃           | 7.22 | 3654 | 3773    | 0.79    | 2.55 |
| BF₂             | 7.22 | 3648 | 3766    | 0.48    | 2.48 |
| P(CF₃)₂        | 7.18 | 3648 | 3766    | 0.69    | 2.51 |
| COOH            | 7.08 | 3648 | 3765    | 0.45    | 2.16 |
| SF₃             | 7.08 | 3649 | 3767    | 0.69    | 2.35 |
| CN              | 7.03 | 3652 | 3770    | 0.66    | 2.21 |
| PF₂             | 6.99 | 3642 | 3759    | 0.59    | 2.28 |
| SO₂CH₃          | 6.97 | 3654 | 3773    | 0.72    | 2.12 |
| COCH₃           | 6.94 | 3645 | 3762    | 0.502   | 2.03 |
| SF₅             | 6.91 | 3651 | 3768    | 0.68    | 2.04 |
| SO₂NH₂          | 6.81 | 3651 | 3768    | 0.57    | 1.93 |
| 5-tetrazolyl    | 6.79 | 3648 | 3765    | 0.56    | 1.78 |
| SiCl₃CH₃        | 6.78 | 3642 | 3759    | 0.39    | 2.03 |
| CO₂C₂H₅        | 6.78 | 3639 | 3756    | 0.45    | 1.93 |
| CO₂CH₃          | 6.76 | 3640 | 3756    | 0.45    | 1.95 |
| PO(OH)₂         | 6.73 | 3648 | 3765    | 0.42    | 1.93 |
| COC₂H₅         | 6.72 | 3640 | 3757    | 0.48    | 2.04 |
| SCN             | 6.71 | 3651 | 3769    | 0.52    | 1.89 |
A. H. Yateem

Table 4. (continued)

| Substituent          | RB (kcal/mol) | pK_a | n_s(NH_2) (cm⁻¹) | n_a(NH_2) (cm⁻¹) | σ_p | SE (kcal/mol) |
|----------------------|---------------|------|------------------|------------------|-----|---------------|
| C≡CCF_3              | 6.70          | 3648 | 3765             | 0.51             | 1.79|                |
| SeCN                 | 6.69          | 3651 | 3769             | 0.66             | 1.84|                |
| SCF_3                | 6.49          | 3649 | 3765             | 0.5              | 1.66|                |
| SiF_3CH_3            | 6.39          | 3647 | 3763             | 0.23             | 1.69|                |
| SCHF_2               | 6.36          | 3642 | 3758             | 0.37             | 1.32|                |
| CF_3                 | 6.34          | 3644 | 3759             | 0.54             | 1.44|                |
| CH(CN)_2             | 6.29          | 3645 | 3761             | 0.52             | 1.41|                |
| CH=NOCH_3            | 6.28          | 3641 | 3756             | 0.3              | 1.30|                |
| CHBr_2               | 6.27          | 3639 | 3755             | 0.32             | 1.24|                |
| COC_6H_5             | 6.14          | 3644 | 3761             | 0.43             | 1.91|                |
| CHCl_2               | 6.08          | 3646 | 3761             | 0.32             | 1.24|                |
| C_F_5                | 6.06          | 3641 | 3755             | 0.27             | 1.08|                |
| B(OH)_2              | 6.06          | 3641 | 3755             | 0.12             | 1.30|                |
| SiH_3                | 5.95          | 3638 | 3752             | 0.1              | 1.09|                |
| CHF_2                | 5.93          | 3633 | 3747             | 0.32             | 1.08|                |
| CCH                  | 5.89          | 3639 | 3753             | 0.23             | 0.87|                |
| CH_2Cl               | 5.78          | 3637 | 3750             | 0.12             | 0.79|                |
| CH_2Br               | 5.77          | 3638 | 3751             | 0.14             | 0.83|                |
| SH                   | 5.69          | 3639 | 3752             | 0.15             | 0.84|                |
| GeH_3                | 5.64          | 3637 | 3749             | 0.01             | 0.76|                |
| Si(CH_3)_2C_6H_5     | 5.64          | 3633 | 3746             | 0.07             | 0.82|                |
| Si(C_2H_5)_3         | 5.64          | 3627 | 3740             | 0.69             |     |                |
| SeCH=CH_2            | 5.62          | 3636 | 3750             | 0.21             | 0.45|                |
| P(C_6H_5)_2          | 5.57          | 3638 | 3752             | 0.19             | 0.87|                |
| I                    | 5.52          | 3.78 | 3638             | 3751             | 0.18| 0.43           |
| SCH=CH_2             | 5.44          | 3637 | 3750             | 0.21             | 0.21|                |
| 2-furyl              | 5.40          | 3633 | 3745             | 0.02             | 0.20|                |
| Br                   | 5.32          | 3.91 | 3638             | 3750             | 0.232| 0.16          |
| CH_2CN               | 5.30          | 3632 | 3745             | 0.18             | 0.36|                |
| Cl                   | 5.16          | 4.15 | 3637             | 3749             | 0.227| -0.04         |
| CH_2OH               | 5.13          | 3623 | 3734             | 0               | 0.00|                |
| H                    | 5.12          | 4.58 | 3632             | 3743             | 0    | 0.00           |
| CH_2COCH_3           | 5.11          | 3629 | 3741             | 0.06             |     |                |
| N=C=O                | 5.02          | 3634 | 3747             | 0.19             | -0.18|               |
| CH_2F                | 5.01          | 3629 | 3740             | 0.11             | 0.03|                |
| N_3                  | 4.80          | 3633 | 3745             | 0.08             | -0.47|               |
| NH_2CN               | 4.43          | 3629 | 3739             | 0.06             | -1.13|               |
| F                    | 4.18          | 4.65 | 3629             | 3738             | 0.062| -1.27         |
Figure 1. Plots of changes of (a) C-NH$_2$ bond distance, (b) H-N-H angle, (c) out-of-plane angle, (d) natural charge on amino nitrogen, (e) minimum ionization potential, and (f) maximum electrostatic potential between the minimum and maximum states versus rotational barrier of para-substituted anilines

Except for 8 structures, it was found that the maximum (positive) molecular electrostatic potential is in the vicinity of the two amino hydrogens (not a particular hydrogen atom) in para-substituted anilines. One can expect that as the electron density is shifted away from these hydrogens, they will have more positive electrostatic potential and that the amino group will be more acidic. Therefore, pK$_a$ values will decrease with the strength of electron-withdrawing groups attached at para-position$^{14}$. The correlation of changes in electrostatic potential and pK$_a$ values with RB have been presented quantitatively in Figs. 1f and 2a, respectively. The order of substituents in terms of strength of electron-donating follows in general that obtained from molecular electrostatic potential analysis$^{11}$.

It was shown experimentally that the force constant, and hence stretching frequency of N–H bond, increases with the increasing power of electron-
withdrawing groups in \textit{para}-substituted anilines. This was attributed to the increasing "\textit{x}" character of the hybrid orbital of the N–H bond relative to \pi-electron charge density on nitrogen atom \cite{33,47,49}. The experimental symmetric and asymmetric NH\textsubscript{2} stretching vibrations of aniline occur at 3373-3396 cm\textsuperscript{-1} and 3460-3481 cm\textsuperscript{-1}, respectively \cite{33,47,49}. The corresponding experimental values for 10 \textit{para}-substituted anilines fall in the range of 3394-3416 cm\textsuperscript{-1} and 3479-3509 cm\textsuperscript{-1}, respectively \cite{33,49,50}. The calculated stretching frequencies here are 200 cm\textsuperscript{-1} more than the experimental values. However, the trend is the same as that observed experimentally; the symmetric and asymmetric stretching frequencies increase with increasing strength of electron-withdrawing substituents and hence with RB. The RB is shown to correlate well with NH\textsubscript{2} stretching frequencies of the minimum states of \textit{para}-substituted anilines (Fig. 2b). For maximum states of \textit{para}-substituted anilines, the stretching frequencies were found to change very slightly. Moreover, this change is not related to the strength of electron-withdrawing substituents due to absence of conjugation in the maximum states.

The correlation of empirical Hammett \(\sigma\) values with RB has been shown in Fig. 2c. The correlation (\(R^2 = 0.852\)) is lower as compared to other parameters, but it is not unexpected considering the reported modifications and corrections to these constants \cite{9,10}. Finally, the stabilization energy is highly correlated to RB as shown in Fig. 2d. The larger stabilization energy correlates to the role of substituents \cite{13}.

### 3.2 \(\pi\)-conjugation and rotational barrier

It was found that the bond between an atom of X attached to benzene carbon (C–X distance) is shorter in \textit{para}-substituted anilines compared to that in the absence of NH\textsubscript{2} group. Moreover, the difference between these two distances in the minimum states increases with RB, ranging from almost 0 to 0.021 Å. On the other hand, as stated above, the C–NH\textsubscript{2} bond distances in \textit{para}-substituted anilines are shorter than that in aniline, ranging from almost 0 to 0.029 Å. This implies that simultaneous presence of aniline, a typical strong electron-donating group, and electron-withdrawing groups causes more shortening of C–NH\textsubscript{2} and C–X bond distances compared to the presence of any one of them.

The shortening of C–NH\textsubscript{2} bond, the increase in planarity of NH\textsubscript{2} group, the decrease in natural charge on N, and decrease in the basicity of NH\textsubscript{2} group in the presence of electron-withdrawing groups indicates that lone amino pair is conjugated with the \pi bond of carbon of benzene ring. The resonance stabilization is extended to substituent X. The decrease in natural charge on amino nitrogen, the increase of minimum ionization and maximum electrostatic potentials, and the increase in NH\textsubscript{2} stretching frequencies with the increasing power of electron-withdrawing substituents further support the electronic delocalization in all the molecules studied here. The fact that these geometric, atomic, and molecular effects correlate strongly with RB, implies that RB is an excellent measure of \(\pi\)-resonance stabilization in \textit{para}-substituted anilines. Moreover, the RB was found to be in good correlation with the empirical constants \(pK_a\) and \(\sigma\). A quantitative scale for the ability of electron-withdrawing groups to \(\pi\) resonance with aniline can be constructed in terms of RB. As discussed \textit{vide supra}, the \(\pi\)-conjugation system is stabilized by the presence of both NH\textsubscript{2} and electron-withdrawing groups in the \textit{para} position. Based on this discussion, one can expect \textit{scheme 1a} to be dominant if RB is more, i.e., the substituent X should be strongly electron-withdrawing. Groups with low RB are presumed to have structures similar to that in \textit{scheme 1b} which is much similar to aniline. It was found that central C–C bond distances of benzene in \textit{para}-substituted anilines are shorter than the lateral C–C bond distances thus supporting the proposed schemes. Substituents with intermediate RB are expected to fall between these two schemes.

By measuring the natural charge on benzene carbon bonded to substituent X, it is found that this carbon becomes more positive as the atom of X attached to carbon is more electronegative, being largest (+0.393) in case of F substituent followed by O atom in OSO\textsubscript{2}CH\textsubscript{3} (+0.225), and then by N atom in NH\textsubscript{CN} (+0.131). RB in case of OSO\textsubscript{2}CH\textsubscript{3} is only 5.33 kcal/mol, and with F and NH\textsubscript{CN}, the RBs have their lowest values, 4.18 and 4.43 kcal/mol, respectively. On the other hand, with substituents of high RB like NN\textsubscript{CN} and N(O)=NN\textsubscript{CN}, the natural charge on C atom bonded to N atom in NN\textsubscript{CN} and N(O)=NN\textsubscript{CN} are only +0.028 and +0.018, respectively. Therefore, the electron-withdrawing inductive effect is expected to have a negligible effect as compared to \(\pi\)-conjugated systems shown here.

This is the first study that quantifies the relation of the electron-withdrawing effect of substituents with RB and correlates the RB barrier to some parameters that are affected by conjugation. It can be considered as a successful alternative quantum mechanical measurement of substituents effects and \(\pi\) conjugation versus the empirical Hammett constants. The opposite atomic, geometrical, and molecular effects were also recorded with several electron-donating substituents in \textit{para}-position to aniline (not shown). A similar study with the same level of
The theory showed that RB is a measure of \( \pi \)-conjugation between the donors NH\(_2\) and OCH\(_3\) with few electron-withdrawing groups in disubstituted 1,3-butadienes \(^{31}\). Strong correlations were also obtained for several geometrical and spectroscopic parameters vs RB for electron-donating substituents in para-position to benzaldehyde (not published yet). Hence, this study is highly likely to be successfully applied to a large variety of different electron-donating and withdrawing substituents to determine their relative strengths.

**4. Conclusion**

The \( \omega \)B97X-D/6-31G** calculations show that the rotational barrier RB between the maximum and minimum states of para-substituted anilines with electron-withdrawing groups is a reliable quantum mechanical measure of \( \pi \)-conjugation in these compounds. The extent of conjugation is verified by several atomic, structural, spectroscopic, and molecular parameters which are shown to be sensitive to substituents and correlate very well with the RB. Moreover, results of the quantum mechanical approach reveal that the RB also correlates well with empirical pK\(_a\) and \( \sigma_p \) constants. Hence, based on RB, a scale for the strength of
electron-withdrawing substituents and their ability to resonate with aniline can be established.

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