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Research Article

G3XMP2 INVESTIGATION OF AMINE INVERSION IN ANILINE AND ITS PARA ANILINES

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ABSTRACT

Objective: This article addresses the inversion dynamics of aniline and para-anilines by G3XMP2 theory and the effect of substituents on the inversion barrier.

Methods: The composite G3XMP2 method is used to evaluate the structural parameter, inversion barrier of aniline and para anilines.

Results: The investigation shows that the electron donating substituents increase the inversion barrier by mesomeric and hyper conjugative effects. Thus it favours a non-planar structure. Electron withdrawing substituents, however, promote the planar structure by strong inductive effects. Of all the ten substituents studied, amino group yields high inversion barrier and results in a non-planar configuration, while the nitroso group attains low inversion barrier and accounts for the planar structure of amine group.

Conclusion: The study concludes that the structure of amine group in aniline molecule is non-planar and its degree of non-planarity is heavily altered by the substituents.

Keywords: Inversion barrier, G3XMP2, Aniline, Amino group, Planarity.

INTRODUCTION

The geometry and inversion of the amino group are of prime importance in DNA base paring and biological interactions. The nucleic acid bases such as adenine, guanine, cytosine, thymine in DNA and uracil in RNA are common components of nucleotides, the building blocks of the nucleic acid strands. These five NA bases can form hydrogen bonds with each other to form base pairs in both double-stranded and single-stranded nucleic acids. The non-planarity of the nucleic acid bases will influence the structure and consequently the molecular recognition of nucleic acids. The nucleic acid bases had been expected to be planar for several years. Accordingly, the theoretical nucleic acid conformational and dynamics analyses assume planar structure for the nucleic acid bases. However, recent ab initio quantum-mechanical investigations have consistently predicted nonplanar configuration of amino groups for the nucleic acid bases [1,2]. It is established by earlier microwave studies that the amino group of aniline is nonplanar and lies at an angle between 37° and 46° from the plane of phenyl ring. Therefore, the high level ab initio investigation of the amino group in aniline and its para derivatives could provide better description about the configuration of the amine group. The amine inversion phenomenon has long fascinated chemists and crystallographers. Hence, the investigations of such phenomena will be extremely useful in drug interactions with its receptor, biological interactions and molecular recognition process. The G3XMP2 composite theory has been used to measure the geometrical parameters and inversion barriers of para-substituted anilines in this study. The computed inversion barriers and geometrical parameters are in excellent agreement with the experimental values [3,4]. The effects of electron donating and electron withdrawing substituents on amine inversion have been studied extensively in this report.

METHOD OF CALCULATION

All the compounds were optimized using the density functional theory (DFT) B3LYP/6-31G (2df, p) level of theory using the Gaussian 03 program [5]. The para-substituted prototype aniline molecules were optimized in both planar and non-planar structures. No geometrical constraints were imposed to obtain the minimum energy structure of aniline and its para anilines. The non-planar configuration of aniline molecule is made by placing the nitrogen atom out of the plane of benzene ring; however, for planar structure the amino group lies in the plane of phenyl ring. Frequency calculations and zero-point energies were calculated using the B3LYP/6-31G (2df, p) level of theory and scaled by the 0.9854 factor. Single point energy calculations were made using QCISD (T)/6-31G (d), MP2/6-311g++ (2df, 2p) and HF/G3XL level of theory. It is necessary to include polarizing functions in the calculation of inversion barriers because of the significant changes in hybridization that accompany with nuclear motions and finally the inversion barrier for aniline and various para anilines were calculated using the composite G3XMP2 [6] theory and its details are available in cited reference.

RESULTS AND DISCUSSION

Structure of the amino group

The most intriguing structural features of aniline and its para derivatives is the determination the configuration of the amino group. The inversion angle (ω) is a vital parameter normally used to measure the pyramidalization of the amino group. It is shown in Fig. 1 that the nitrogen atom of the amino group is tilted slightly from the ring plane, and the two amino hydrogen atoms are deviated from the nitrogen plane, the inversion angle (ω) is denoted as "a," out of plane angle (δ) is denoted as "b" and tilt angle (ϵ) is denoted as "c." The microwave analysis of aniline [7] is based on the assumption that the entire ring is perfectly planar; however, both the electron diffraction results[7] and X-ray analysis [8] shows that the amino group is located out of plane of the benzene ring.

The deviation from planarity is due to the pyramidalization of amine nitrogen. The asymmetric interaction between the amino group and the benzene ring causes a minor displacement of the nitrogen atom from the plane of benzene ring, and it is denoted as the tilt angle (ϵ). The substitution of electron withdrawing substituent widely opens the H-N-H bond angle and attains planar configuration [9]; this effect is particularly pragmatic for the -NO, -CN, -NO2 and -CHO substituents. The inversion angle computed by G3XMP2 theory for aniline molecule is 50.71° and this closely resembles with the experimental values of 48±2° and 42.4±0.3° obtained by microwave spectroscopy [10]. This

close agreement reveals that the optimized structure of aniline using B3LYP/6-31G (2df, p) basis set is effective in producing the equilibrium geometry structure of aniline. Electron withdrawing substituent such as -NO_2, -CN -NO and -CHO decreases the tilt angle from 2.86° to 2.37°, 2.47°, 2.35º and 2.49° and consequently leads to the planar form. Electron donating substituents such as methyl and the hydroxyl group augments the out of plane angle from 2.86° to 3.07°, 3.17°, and promotes the non-planar amine structure.

Amine group inversion

The inversion phenomenon of the amine group is shown in Fig. 2. The complete planar structure of the entire aniline molecule maximizes the interaction of nitrogen lone pair with phenyl ring [11].

The C-N bond length of aniline molecule has the value of 1.3762 Å in its planar form, and the value is very close to the 1.376 Å of formamide, in which amino group is perfectly planar. The non-planar structure of the aniline molecule shows one imaginary frequency in frequency calculations, which confirms the presence of a planar structure of aniline. The characteristic inversion frequency of the amino group in aniline molecule is 462.04/cm scaled by the Zernike phase contrast (ZPC) scale factor 0.9854 [12]. The calculated inversion barrier height for the aniline molecule with ZPC is 6.0 kJ/mol which is parallel to the experimental value of 6.3 kJ/mol obtained by microwave and infrared spectra [13,14].

Effect of electron withdrawing substituent

The role of substituent in aniline molecule plays a central role in determining its structure, and inversion parameter [15,16]. Tables 1 and 2, shows the geometrical and structural details of para aniline derivatives. The structure of para aniline derivative is shown in Fig. 3.

It is interesting to note that planarity of the amine group is favored by the electron-withdrawing substituent. The substituent such as nitro group drastically reduces the inversion barrier to half the value of aniline from 500/cm to 220/cm. Introduction of nitro, cyano, nitroso and aldehyde group at the para position of aniline makes the molecule more planar by resonance and delocalization of π electrons around the phenyl ring. It is clear from Fig. 4 that the increase in C-N bond length increases the inversion angle and accounts for pyramidal configuration of the amine group. Among the 10 selected aniline para derivatives, nitroso aniline is the only substituent makes the molecule more planar by shortening the C-N distance from 1.397Å to 1.370Å with the barrier height of 205/cm. On the basis of resonance theory, electron-withdrawing substituents, especially at the para position promotes

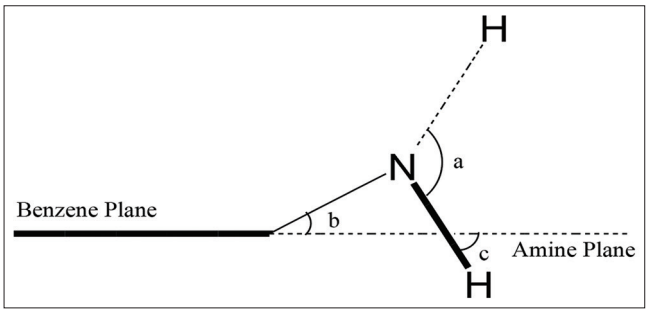

Fig. 1: Structure of amine group

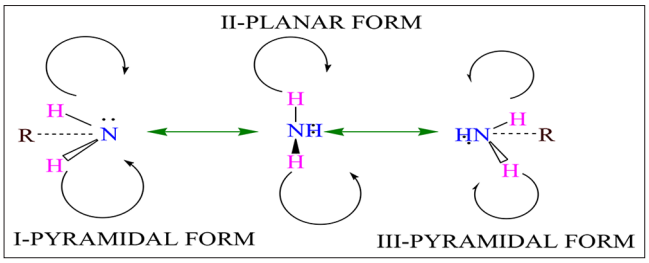

Fig. 2: Inversion process of the amino group

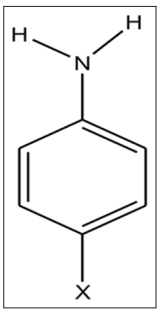

Fig. 3: Structure of para aniline, X-substituents

Table 1: Inversion barrier of para substituted aniline

S. no.	Para substituents (x)	Inversion barrier/cm	Inversion barrier*/cm
1	-H	487.50	499.23
2	-F	475.17	457.79
3	-NO_2	229.67	220.86
4	-CN	299.25	298.48
5	-Cl	489.37	501.12
6	-COOH	308.49	308.86
7	-CH_3	563.58	578.48
8	-OH	677.66	692.35
9	-CHO	280.75	284.21
10	-NO	212.27	205.34
11	-NH_2	719.62	738.81
12	-OCH_3	672.40	694.25

*Scaled parameters

Table 2: Structural parameters of para aniline derivatives

Substituents (x)	H-N-H angle in degrees	d (C-N) Å	Inversion angle (ω) (Degrees)	Tilt angle (ϵ) (Degrees)	δ angle (Degrees)
H	111.168	1.397	42.35	2.5	44.85
-F	110.630	1.400	43.79	2.661	46.451
-NO_2	113.861	1.378	32.84	2.04	34.88
-OH	109.994	1.406	45.70	2.70	48.40
-CH_3	110.890	1.399	43.226	2.5134	45.74
-CN	113.265	1.382	23.65	2.12	25.771
-COOH	113.054	1.383	36.08	2.159	38.239
-Cl	111.443	1.390	41.48	2.49	43.97
-NO	114.262	1.370	31.16	2.35	33.24
-CHO	113.425	1.380	23.65	2.12	25.77
-NH_2	109.680	1.400	46.56	2.83	49.39
-OCH_3	110.066	1.400	45.634	2.74	48.374

quinoid resonance structures, which are more planar than the parent aniline molecule [17]. Table 1 clearly depicts the low inversion barrier for nitroso, nittro and cyano aniline, this illustrates that π electron delocalization in the phenyl ring favors the planar configuration during the inversion process [18]. Electron withdrawing substituent makes the ring electron deficient by negative inductive effect and disperses the electron density cloud around the nitrogen atom, thus promotes a planar configuration.

The symmetric interaction between the amino group and phenyl ring plays a cardinal role in promoting planar configuration of the amine group, and it causes C-N bond to attain partial double bond character. Electron is withdrawing substituents -NO and -CN group forms partial double character of C-N bond to attain the planar configuration. The computed out of plane angle (δ) value for para fluoro-aniline is 46.45°, which agrees well with the experimental value of 46.22° determined by microwave spectroscopy [19] and this authenticates the accuracy of the G3XMP2 theory. Table 2, perfectly signifies that the substitution of both chlorine and fluorine at the para position of aniline does not make a significant change in the geometrical features. In general, halogens at the para position of aniline interacts with the ring by mesomeric and inductive effects, does not cause significant change in inversion geometrical parameters.

Effect of electron donating substituents

Electron donating substituents generally enhances the flow of electrons into the benzene ring with a concurrent increase in electron density around the nitrogen atom and inversion barrier [20]. The methyl group at the para position enormously increases the inversion barrierto 563.58/cm. due to high electron density on the amine nitrogen by hyper conjugative effects. Besides, the DFT studies revealed that the substitution of the methyl group on the benzene ring causes a reorganization of the π electron along the ring with the corresponding increase in electron density around the nitrogen atom and causes non-planarity of the amine group. The experimental inversion barrier height of the para methyl aniline determined by gas phase infrared spectroscopy [21] is 588/cm which is in excellent agreement with the calculated value of 579/cm. Substitution of the hydroxyl group at the para position of aniline increases the electron density around nitrogen of the amino group and consequently increases the inversion barrier height to the large extent of 692/cm among the 10 selected para derivatives. The out of plane angle (δ) for the para hydroxyl aniline is 48.4° that is the highest value among the 10 selected aniline para aniline derivatives, and this makes the ring non-planar. It can be delineated by the fact that enormous flow of electron from the hydroxyl group places high electron density around nitrogen and causes asymmetric interaction between carbon and nitrogen.

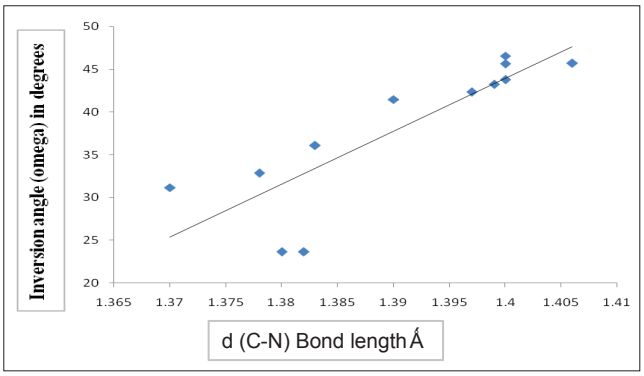

Fig. 4: Correlation between inversion angle and bond length

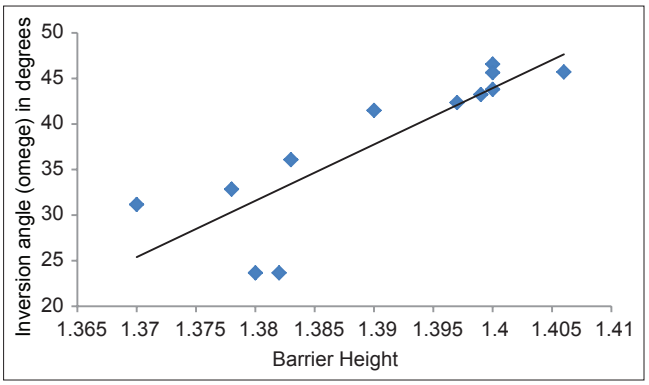

Fig. 5: Correlation between inversion angle and barrier height

It is apparent from Fig. 5 that the inversion barrier is directly proportional to the out of plane angle and hence, this relationship authenticates the non-planarity of the amine group in para methyl and para hydroxy aniline. Contrary to the electronegative substituents, the electron donating substituents lengthens the C-N bond by causing asymmetric interaction between nitrogen and phenyl ring. This strong interaction distorts the rings to the greater extent and places nitrogen atom out of the plane by 2.7° from the phenyl ring plane. This phenomenon causes transformation of partial double bond character to pure single bond character, which causes non-planarity of the amine group. Similarly, the substitution of the methoxy group at the para position also accounts for higher inversion barrier due to the high inversion angle of 48.37°. It is apparent from Table 2 that the optimized geometrical parameters and computed values for the electron donating substituent accounts for substantial distortion of phenyl ring and places the amine group away from the ring plane. The deviation of the amine group from the ring plane causes non-planarity of the structure. The substitution of the amino group at the para position of the aniline drastically increases the inversion barrier height to 739/cm. The measure of pyramidalization of the amino group for para diamino benzene is the largest among the electron donating substituents, and it has the inversion angle of 46.56° and tilt angle of 2.83°. The large deviation from the planarity of the amine group for para di amino benzene is mainly due to increase in electron density around the nitrogen atom. Hence, the substitution of the amino group at the para position makes the molecule completely non-planar. In general, the substitution of electron donating groups at the para position increases the C-N bond length due to the asymmetric interaction between the nitrogen atom and phenyl ring. However, it decreases the H-N-H bond angle and accounts for the non-planar configuration of the amine group.

CONCLUSION

The investigation of geometrical parameters and inversion barrier of 10 para aniline derivatives using the G3XMP2 theory is established in this report. The analysis concludes that the introduction of substituents at the para position of aniline has substantial effect on inversion barrier and configuration of amine group. The inversion angle (ω), tilt angle (ϵ), the out of plane angle (δ) and the inversion barrier height are the key parameters employed to interpret the planarity and non-planarity of the aniline ring. In a nutshell, it has been found that the lengthening of the C-N bond increases linearly with an increase in pyramidalization of the amino group, inversion angle (ω), tilt angle (ϵ) and thus apparently results in a non-planar configuration. The lengthening is due to the asymmetric interaction between amine nitrogen and phenyl ring. However, the substitution of electron withdrawing substituents at the para position of the aniline molecule decreases the inversion angle, tilt angle, out of plane angle and consequently decreases inversion barrier height with definite planarity of the amine group in aniline molecule. Electron withdrawing substituents generally decreases the degree of pyramidalization by strong electron delocalization and resonance phenomenon, thus imparts for planarity of aniline molecule. This G3XMP2 investigation of amine inversion provides promising information about the geometrical parameters, inversion barrier, planarity and non-planarity of aniline molecule. The computed values for amine inversion agree well with experimental values and hence, these findings will have potential applications in DNA base pairing, biological interactions, pharmaceutical applications and molecular recognition process.

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