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Systematic Computational investigation on change of Mulliken charge assignment, HOMO-LUMO interaction, ^{13}C NMR chemical environment by sequential substitution of amino group on naphthalene ring

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ABSTRACT

The mulliken or molecular charge distribution deeply describes the 3D spatial distribution of anisotropy electron density over the molecule. The mulliken charge around the molecular sites can be operated by donation and back donation of electrons around the atoms due to the influence exerted by attached atoms or molecule as substitutions. The manipulation of electron cloud in different molecular site and the rate of electronegativity and protonic-positivity of the atom were traced. Ultimately, the required energy to isolate the electron density in the atomic site was measured. By such application, the necessary electronic energy to bind the atom with the regular molecular sequence was estimated. The change of chemical environment of carbon in the molecular chain due to the addition of substitutions was monitored by which the chemical shift was measured and shift was calibrated.

Key words: 3D spatial; anisotropy-electron density; protonic-positivity; electronegativity; chemical shift.

INTRODUCTION

In the molecular formation, the atomic orbital community is concurrently changed as molecular orbital community. The molecular orbitals (MOs) are build up by individual atomic orbitals chain and the orbitals with same energy coincide with one another by

electronic interactions and generally formed as localized and delocalized system [1, 2]. The localized orbital generated with periodic boundary conditions called as wannier functions also known as specific bond or lone pair of specific atom whereas the delocalized is formed by the distribution of electron density beyond a boundary conditions [3]. The delocalized electrons are generally distributed with respect to the electrophilic and nucleophilic influence of respective atoms in the molecule and the unitary transformation is maintained among the atoms whereas localized electrons are preserved between the atoms and polarization and diffusional functions limited as per the DFT theory. Nevertheless, the localized electrons are usually dominated by the asymmetrical forces exerted by the respective atoms and also little bit influenced by the attractive and repulsive forces existed on the nearby atoms.

In the molecular formation, the electrons are oriented themselves in the direction according to the spatial boundary conditions. However, the electrons are reoriented on different places of the molecule within the limit of HOMO and LUMO and are correlated by the attractive and repulsive pressure among the atoms. So the density of electrons is asymmetrically distributed at the molecular site and the gradient of the concentration depends on the molecular-electrochemical forces. Such electrochemical forces born from the energy fraction generated in the chemical reaction. It can be classified in two categories depends on the energy exchange in the chemical reaction such as endothermic and exothermic. The energy of these two reactions, the electro-chemical energy is restored in the molecular site. Until the chemical end of the reaction, the energy absorption or energy transmission usually continued known as Gibbs energy [4,5].

The localized and delocalized electrons making unequal charge distribution within the boundary and among the molecular site respectively known as mulliken charge gradient. Apart from that the gradient of charges, such as electrophilic and nucleophilic is usually elaborating impact of substitutions on the main core of the molecule [6,7]. Then, from the impact, the charge gradient change, chemical potential modification, molecular charge moment, energy required to receive the substitution by the main core of molecule, chemical environment change, chemical energy stored in nodal points of the molecular site etc., can be measured and thereby change of chemical properties can also be studied. Nowadays, it is very important to understand the fundamental properties and the calibration of properties by known base and substitutional compounds to synthesize drugs, functional materials, digital electronic materials, and high frequency operated devices for multi-phase applications. In this case, in naphthalene core, the amino group is added in all positions including ortho, meta and para, on both sides of benzene frame and the charge gradient change was estimated

COMPUTATIONAL METHODS

The GAUSSIAN program run for obtaining and generating optimization of structure, energy calculations and NMR spectral data using B3LYP/6-311++G(d,p) methods. According to the DFT theory on literature reports [8], this type of basis set make available accurate values and it is capable to harmonize to experimental data. At this point, in the

computational calculations, no symmetry has been enforced during the optimization of molecular structure. The electronic energy excitations were carried out using TDDFT methods on internal molecular structures [9,10]. The molecular structure in ground state was constructed using major calculative method of HF and DFT and all the computations were performed by Gaussian 16 in IMAC computer.

RESULTS AND DISCUSSIONS

Mulliken charge configuration analysis

The amino group is substituted sequentially on all the C of the naphthalene ring and the mulliken charge levels are measured and monitored and furnished in table 1. The amino at first position in naphthalene creates negative population of electrons around the core CC which are forcefully occurring by the electron withdrawing group. In the ring side, except C3 and C4, all the core CC are populated by the molecular electrons (unpaired). The electronegativity of the C11 is -0.737 eV which is very high when compared with all the rest of CC. At the same time, the electronic gradient at N is -0.365 eV and this is one half of the C11 of the ring. Apart from C3 and C4, the electron clouds are occupied irrespective of C at ortho, meta and para positions. It is the symmetrical displacement paddle of electrophilic architecture about the center of the naphthalene. Simultaneously, internal energy of the molecular system rather differed when compared with pure naphthalene compound.

Table 1: Mulliken charge levels according to the amino positions

Atoms	Amino position in naphthalene							
	1	**2 ortho**	**3 meta**	**4 para**	**5 para**	**6 meta**	**7 ortho**	**8**
C11	-0.737	0.198	-0.035	-0.642	-0.133	-0.144	-0.264	-0.315
C14	-0.409	-0.350	-0.354	-0.264	-0.397	-0.338	-0.384	-0.558
C15	-0.249	-0.342	-0.291	-0.401	-0.553	-0.390	-0.345	-0.400
C10	-0.643	-0.020	0.164	-0.750 (C9)	-0.480	-0.177	-0.173	-0.068
C2	-0.167	-0.130	-0.177	-0.480	-0.750	0.164	-0.422	-0.439
C1	-0.422	-0.341	-0.390	-0.553	-0.401	-0.291	0.247	-0.414
C6	-0.517	-0.390	-0.338	-0.397	-0.264	-0.354	-0.251	-0.064
C5	-0.503	-0.182	-0.144	-0.133	-0.642	-0.035	-0.610	-0.250
C3	0.765	0.095	0.037	1.462	1.462	0.037	0.304	0.615
C4	1.440	0.020	0.108	0.715	0.715	0.108	0.459	0.420
N	***-0.365***	***-0.378***	***-0.386***	***-0.358***	***-0.358***	***-0.386***	***-0.374***	***-0.413***
H19	***0.294***	***0.284***	***0.279***	***0.292***	***0.243***	***0.279***	***0.243***	***0.260***
H20	***0.242***	***0.249***	***0.246***	***0.243***	***0.292***	***0.246***	***0.276***	***0.274***

When amino group at ortho position, the electronegativity of C14 is -0.350 eV and C15 has almost same value. The neutral atmosphere is always generated by equal massiveness of the electronegative and protonic-positive contents.

Here, the neutral point is found at C4 and C10 where two opposite regions are separated. Except C1, C6, C14 and C15, the major part is covered by the protonic content. So, there is no further alternation is found and the internal energy is not spent so much. This view showed the meagre amount of internal energy is spent to receive the amino group at ortho position. The amino at meta position, the previous energy distribution is not altered much and neutral atom is appeared at C11.

The charge negativity of amino on core (C14) is – 0.291 eV whereas the adjacent C15 is charged by -0.354 eV. The C9 is populated by negative gradient of -0.750 eV due to the amino position at para position. In this atmosphere also, the more number of core CCC is populated by electron clouds. The neutral atom is found at C5 at the left top of left moiety and as the first case, except center, all the core CC are coherent electronegativity.

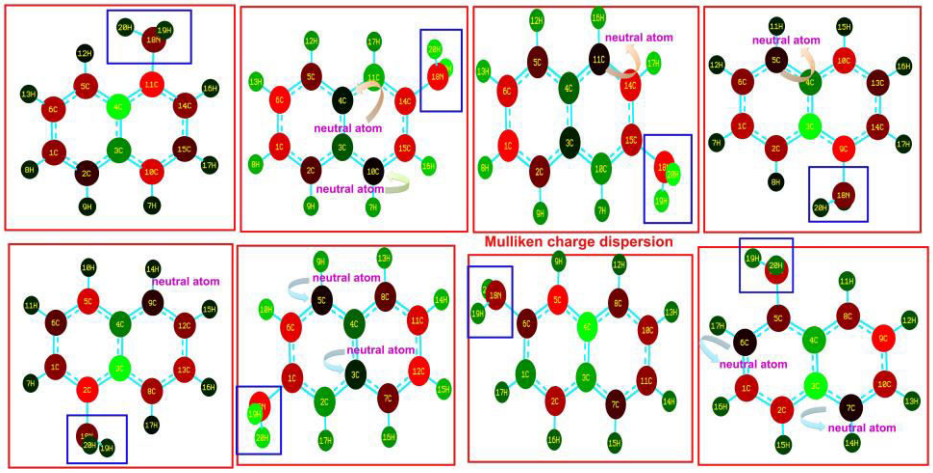

Figure 1: Amino groups

As in the figure 1, the amino group at para position on left moiety, C2 is valued electro negatively by -0.750 eV and the neutral atom is appeared at C9. In this case also, all the CC is surrounded by electronic gradient of charges. As usual, the center position of the ring is protonically populated. Hence, the amino at meta position, the C1 is influenced by -0.291 eV whereas C3 & C5 become neutral about which the electronic and protonic regions

are isolated. Since the amino position is at ortho, the electron cloud is moved apart from the amino group and except C5 (-0.650 eV), the electrophilic zones are reduced much. Especially, there is no neutral atom is observed in this mulliken configuration.

Continuously, the NH_2 at first position of left moiety, the subsequent atom (C6 and C7) is neutral and C9 is more populated by -0.558 eV. From this observation, it is clear that the negative and positive zones of charges are distributed asymmetrically and the charge zones are balanced with respect to substitution. However, by the application of the modification of electrochemical forces among the atoms of the molecular site, the mulliken charge heterogeneity causing the change of chemical potential from pure naphthalene to amino naphthalene.

Energy modulation on substitution

Each and every molecular system has its own internal energy to assemble together by the application of exothermic process. According to the law of conservation of energy of the organic system, the internal energy is conserved for all molecular formation and as per the law of thermodynamics, the laws are satisfied and definitely the chemical reaction obey the thermodynamic energy relation [11,12]. In the case of naphthalene compound, the internal energy of 10433.670907 eV is spent to assemble 18 atoms in a hexagonal frame work of carbons. The internal energy usually extended by the substitution with number of atoms in symmetric and asymmetric sequential pattern. Accordingly, when the amino group is added at all the position of H atom and the energy is monitored. The change of internal energy of amino-naphthalene compound is depicted in Table 2. As in the Figure 1, for substituting the amino group at first position, required energy was 11931.20490541 eV.

Table 2: Internal energy change on amino position

Amino position	Energy in eV	Dipole moment Debye	Energy change in eV
Raw	10433.670907	0.00	Ref.
1	11931.20490541	1.363	12.64499
2 ortho	11931.37189723	1.197	12.81198
3 meta	11931.42391058	1.214	12.86399
4 para	11931.28899412	1.376	12.72908
5 para	11931.28899330	1.376	12.72908

6 meta	11931.42391113	1.214	12.86399
7 ortho	11931.42218185	1.438	12.86226
8	11931.41683755	1.279	12.85692

Additionally, 1497.534 eV amount of energy was spent to fix amino group at first position. Whereas, when it second position i.e. in ortho position, 11931.37189723 eV was needed to create the compound. Here, 12.64499 eV energy additionally required to compose. To fix the amino group at meta position, 11931.37189723 eV is required and 12.81198 additionally spent to make a compound. When amino at para position, 11931.28899412 eV energy is essential and 12.72908 eV additionally spent. The above all described the amino position at ortho, meta and para position in right moiety of naphthalene. Similarly, the amino at respective positions on left moiety, the related energy was measured for each case and it was 11931.28899330, 11931.42391113, 11931.42218185 and 11931.41683755 eV respectively. For that, the energy modulation for each case was 12.72908, 12.86399, 12.86226 and 12.85692 eV respectively.

The compound without substitution, the dipole moment is almost zero and the compound is symmetrically balanced. But, with substitution, the dipole moment was varied from 1.197 to 1.438 dyne. Irrespective of amino group on left and right moiety, the dipole moment is almost same. But amino at ortho on left moiety, the dipole moment was 0.241 dyne was higher when compared with amino at ortho on moiety. The overall observation describes that the minimum energy is required to fix the amino group at para position irrespective of left and right moiety.

HOMO-LUMO interaction analysis

The molecular orbitals are justified by the linear combination of atomic orbitals (sum and the difference of two wave functions) that always existed with respect to the assignment of electronic energy dispersion. Until the energy equivalence satisfied among the electrochemical forces, the electron clouds reassigned on molecular orbitals on the axis and out of the axis of nuclei. The molecular orbitals are overlapped with one another wherever the same energy found among the orbitals.

Apart from that, the electrons with different energy are arranged in different modes of orbital interaction. Such as in phase and out of phase interaction. In in-phase, resulting electron–nucleus electrostatic attractions enforced to reduce repulsion between the respective nuclei and the atomic orbitals or orbital lobes with same sign interact to one another and it gives improved electron probability between the nuclei by the application of constructive reinforcement of the different wave functions. In out of phase, orbital are generally found in the space outside the inter-nuclear region with same or different energy, then the repulsion taking place between nuclei. Thereby atomic orbitals or orbital lobes of opposite sign interact to give reduced electron probability between the nuclei due to destructive reinforcement of the wave functions of individuals called antibonding molecular orbital. The energy assignment between two such orbitals (HOMO-LUMO) is manipulated with respect to the internal energy of base and substitutional groups. If the single bond and its non bonded electrons related orbital interaction taking place, it will be called as σ-bond interactive system. If the interaction taking place between π-bonded system and hybrid bonded system, it will be treated as π-interactive system. If interaction is taking place among more than two interactive systems, it will be known as δ-interactive system. Mostly, such type of interaction appeared over degenerative orbital system of organized molecular orbitals. All these orbital overlapping complex system is usually appeared irrespective of HOMO and LUMO.

Table 3: Energy gap of amino-naphthalene at different position

Amino position	HOMO	LUMO	Energy difference	Energy gap in eV
1	0.2736	0.03688	0.23672	6.4414
2-ortho	0.2782	0.03374	0.24082	6.5530
3-meta	0.2790	0.03374	0.24161	6.5745
4-para	0.2778	0.03704	0.24083	6.5533
5-para	0.2778	0.03704	0.24083	6.5533
6-meta	0.2790	0.03747	0.24161	6.5745
7-ortho	0.2778	0.03713	0.24071	6.5500
8	0.2729	0.03754	0.23542	6.4061

In this case the naphthalene compound is adopted with amino group and change of energy between HOMO and LUMO is monitored and is presented in the Table 3. The orbital energy interaction for HOMO and LUMO portray is displayed in Figures 2 & 3. As in the Figure 3, irrespective of different positions of amino group in naphthalene ring, π-bonding

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interactions are formed in HOMO system. Whereas in LUMO, depends upon amino group, the 3D space orbital interactive system appeared around the hydrogen atom.

Except that, some empty orbital system is appeared to receive excited electrons from the HOMO complex. The electro-chemical interaction justified by means of transition of electron cloud between HOMO and LUMO and it provide against the chemical properties of the compound.

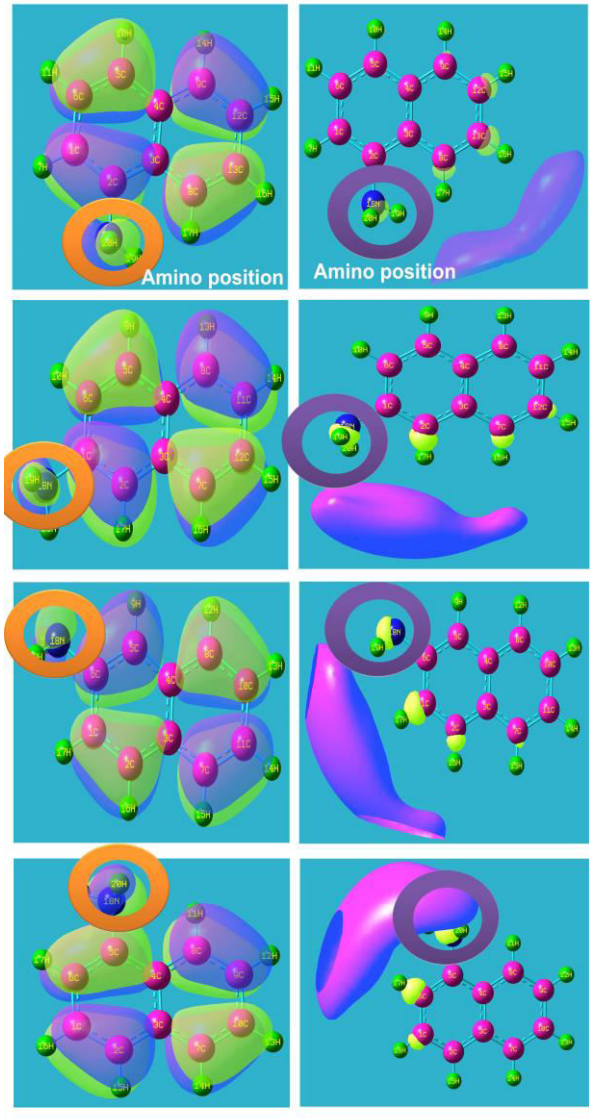

Figure 2: HOMO

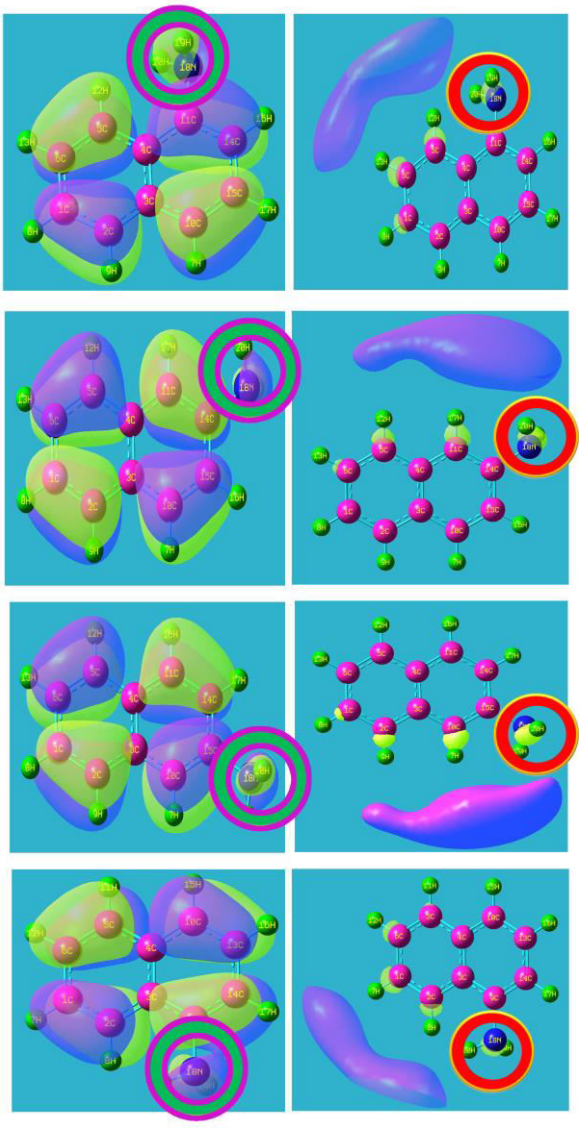

Figure 3: LUMO

For the present compound, all the HOMO and LUMO diagrams make sense the different positions of amino group. As it is composing of two benzene ring, the amino group

is substituted in two ortho, meta and para positions and simultaneously, the energy gap change with respect to the positions have been calculated. Here, in two ortho positions on left and right moieties, the same energy gap (6.5530 and 5.5500 eV) is observed where 0.0030 eV is higher at left moiety than right moiety. In first position on two moieties, the energy gap is 6.4414 and 6.4061 eV respectively and here 0.0353 eV differed between two moieties. When at meta position, the large energy gap (6.5745 eV) is observed and it is most higher than rest of all. Same energy gap of 6.5533 eV is obtained at para for both moieties.

NMR observation

The carbon chemical shift is usually manipulated by the type and place of substitutions in the aromatic ring system. When the aromatic ring itself has specific chemical shift and it is generally ranged from 20 ppm to 100 ppm due to the uniform deshielding effect on core carbons by the effect of hydrogen atoms.

Due to the additional atoms or molecule as substitution, the carbon related to substitution is deshielded further and up field range 120-180 ppm. Here, the base of naphthalene is substituted by the amino group in different positions and the chemical shift is calculated theoretically.

The Table 4 showed detailed chemical shift of carbons by the application of amino group. The ordered chemical shift of all carbons in terms of amino group is presented here that explicit the clear picture of chemical environment of the core carbons in the ring.

Table 4: ^{13}C NMR chemical shift by amino substitution

Amino position	Right moiety								Left moiety							
	1		2 Ortho		3 Meta		4 Para		5 Para''		6 Meta''		7 ortho''		8	
	C11		C14		C14		C9		C2		C1		C6		C5	
Chemical shift (ppm)	158		160		160		156		156		163		160		156	
Associated C atoms	C4	C14	C11	C15	C11	C15	C3	C14	C1	C3	C6	C2	C1	C5	C4	C6
Chemical shift (ppm)	135	138	139	140	131	135	135	135	135	135	131	123	138	137	135	137

When amino at first position, the chemical shift of respective carbon is 158 ppm at right and 156 ppm at left respectively. The chemical shift of nearby carbons is 135 and 138

ppm at right and 135 and 136 ppm at left moiety respectively. At meta position the chemical shift of concern carbon is 160 and 163 ppm on right and left moiety respectively. The chemical shift of associated carbons is 131 &135 ppm and 131 & 123 ppm respectively.

The carbons on right moiety have more influenced than left moiety which is due to the energy difference between them and it is evidenced from Table 3. In the case of para, the chemical shift is same (156 ppm) on both sides and also same (135ppm) on associated carbons. From this observation, it is clear that, the chemical shift of carbons is fluctuated due to the energy interaction effect on core carbons by the amino adoption.

CONCLUSION

By knowing the energy manipulation by known compound, the chemical energy change by unknown species can be studied. Form the observed energy, the required energy level to facilitate the desired chemical properties can be quantified. The geometry, mulliken charge assignment modification, chemical energy and HOMO-LUMO interaction force changes are monitored from the computational calculation made over the amino group substituted naphthalene compound. The base mulliken charge configuration alternation is structurally monitored from which the change electronegative and protonic content movement on the molecular site is ensured. The charge displacement vector alignment on ring by each and every position of amino group is keenly observed and respective production of neutral atom confinement on specific atoms in the ring is studied. The existence of HOMO-LUMO interaction is displayed from which the change of band gap energy is found. The critical point of in-phase and out of phase interaction is observed due to which the hybrid orbital interaction is analyzed.

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