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Theoretical Investigations of Polyaniline with increased number of monomers

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Abstract

Polyaniline polymerization mechanism has been studied theoretically using semi empirical quantum mechanical Hamiltonian Intermediate Neglect of Diffraction Overlap-1 (INDO1/S Singlet spectra) and the basis set STO 6G. The geometric optimization has been using three different semi empirical models Austin Model-1 (AM1), Parameterized Model 3 (PM3) and Modified neglect of diatomic overlap (MNDO). Heat of formation, dipole moment, optical band gap energy for the transition from Lowest Unoccupied Molecular Orbital (LUMO) to Highest Occupied Molecular Orbital (HOMO) and core repulsions have been calculated from the models with increased number of monomers in the chain.

Introduction

One of the principle of condensed matter physics to establish a relationship between structure and properties of the materials and could be achieved by using the quantum computational methods. The theoretical predictions are useful to obtain the stable molecular structures, to know the thermodynamic nature and predict molecular properties such as spectroscopic transitions, optical absorptions [1], Vader wall's interactions and coupling between nuclear and electronic degrees of freedom [2,3] Many quantum computational program packages are available, some of which are available with free license for academic and research purpose, Arguslab is one of such softwares, checked and verified for geometric optimizations of molecules [4,5]. The present study has been carried out to study the variations in heat of formation, dipole moment, band gap energy and the core repulsions, of polyaniline by increasing the chain length by adding one monomer at once, theoretically using arguslab.

Polyaniline is a well-known and extensively studied electrically conducting polymer since its discovery in the 19th century [6-9]. Initially it was grown as a thin film and later on nanowires were developed under certain controlled conditions [10]. The ability of growing it one dimensionally make it different than other conducting polymers and have an advantage in nanoscale devices [11]. Polyaniline has a wide range of applications such as chemical sensors, battery electrodes, super capacitors, display devices, fuel cells and anticorrosion coatings.

The present study will be supportive to understand the mechanism of polymerization of aniline to polyaniline. The results may be utilized to study the modifications in the properties of the polymer with the increase in the chain length, as polyaniline hasn't been studied much theoretically.

Methodology

The molecular modelling of Polyaniline has been performed using Arguslab [12-14] by varying the number of monomers between 0 to 6 in the polymer. Semi empirical quantum mechanical Hamiltonian Intermediate Neglect of Diffraction Overlap-1 (INDO1/S Singlet spectra), the basis set STO 6G and the Universal Force Field (UFF) has been utilized for the molecular modelling and geometric optimizations. The geometry of the polymer has been optimized thrice using three different semi-empirical models of quantum computation MNDO, AM1 and PM3 to compare the results of three computational methods on an IBM computer. The conventional bond separations and bond angles obtained in literature have not been applied before the geometrical optimization of the polymer. Heat of formation, Dipole moment, optical band gap energy corresponding to HOMO-LUMO transition and Core repulsion have been calculated. The structures obtained after geometric optimization for different polyanilines with n varying between n=0 to 6 have been shown in figure 1(a-f)

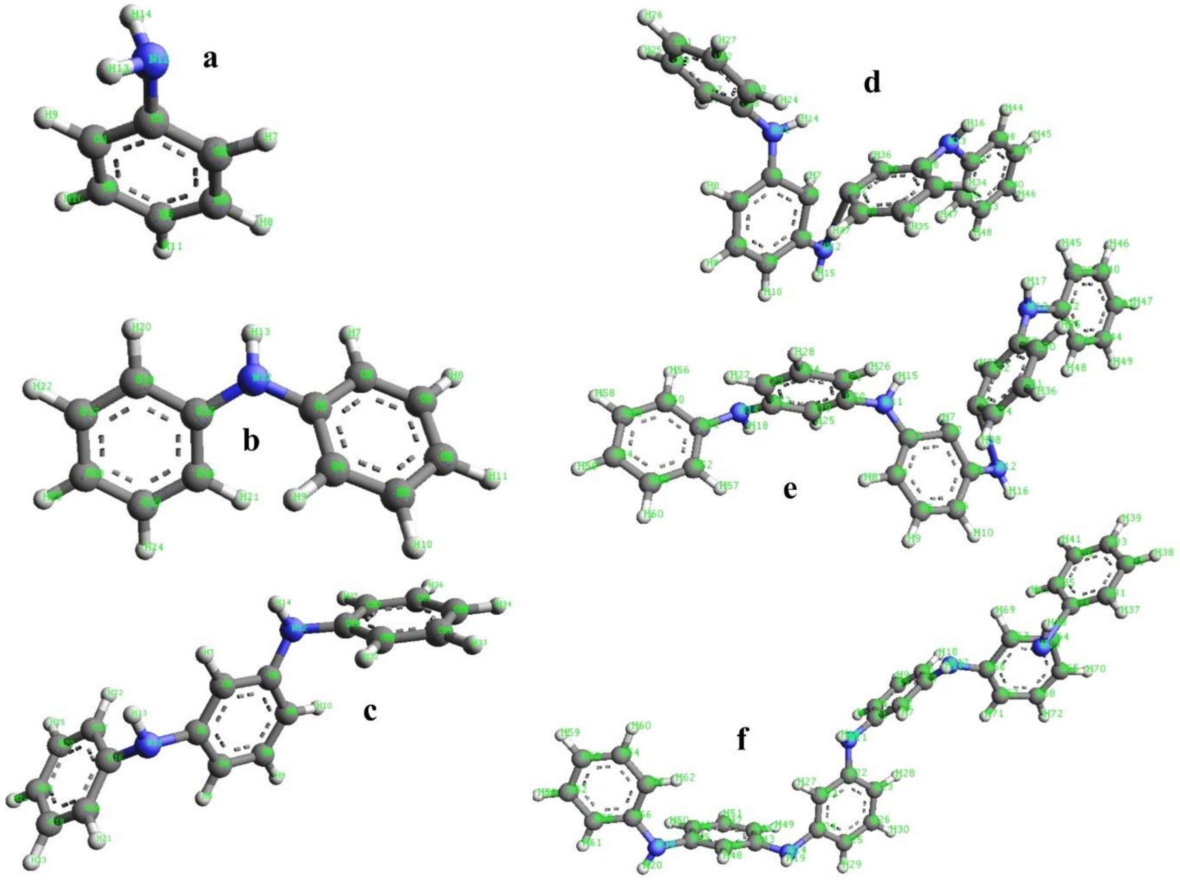

Figure 1 (a-f): Polyaniline structures with n varying between 0 to 6

Results and Discussion:

The results of variations in heat of formation for polyaniline molecules with varying number of monomers using different semi-empirical methods AM-1, PM-3 and MNDO have been reported in table 1. The enthalpy has been found to increase linearly with increased number of monomers and is found to be minimum for MNDO semi-empirical method. The increase in the enthalpy can be attributed to the increased number of aniline monomers, as more heat is required to add more number of monomers to the polymer. The enthalpies have been found to be maximum forPM3 Model. The results of AM-1 and MNDO resembles to a larger extent as compared to PM-3.

Table 1: Variations in Heat of Formation of polyaniline with increasing number of monomers using AM-1, PM-3 and MNDO

No of monomers(n)	**AM1 (Kcal/mol)**	**PM3 (Kcal/mol)**	**MNDO (Kcal/mol)**
1	25.7775	26.3129	24.9211
2	58.4107	53.0500	58.0248
3	93.8007	81.3424	92.7213
4	146.3594	132.5300	145.7563
5	181.9562	160.9790	180.6015
6	238.7420	203.5457	224.6220

The dipole moment of polyaniline in its ground state with varying value of n have been calculated using the three methods and the results obtained are reported in table 2. The dipole moment has been observed to decrease upto n=3 and then increases abruptly. The dipole moment in polymers arises due to two reasons, the first is the separation between the centre of positive and negative charges whereas the second is due to the displacement of charge densities on the atoms constituting the polymer due to mixing of atomic orbitals and the orientation polarization. Thus the increase in dipole moment may be attributed to the steric hindrances in the polymeric chains. The results of PM-3 and MNDO again have been observed to provide similar results for dipole moment [15].

Table 2: Variation of Dipole moment with increasing number of monomers

No of monomers (n)	**AM1 (Debye)**	**PM3 (Debye)**	**MNDO (Debye)**
1	1.35	1.21	1.35
2	1.16	1.44	1.45
3	0.74	0.32	1.82
4	3.99	6.92	7.08
5	4.55	5.60	7.34
6	11.64	9.55	9.18

The optical band gap energy of the polymer with increased chain length has also been calculated for the respective transition for HOMO-LUMO and have been reported in table 3. The energy has been detected to decrease with increased number of monomers up to n=4 and decreases thereafter. The optical band gap of organic molecules depends on the bond length alteration configuration, planarity, aromaticity [16,17] and are useful in describing certain trends in variations in bandgap structure of polyaniline depending on the electronic structure of macromolecules [18,19].

Table 3: Variation of optical band gap energy corresponding to HOMO-LUMO transition with increasing number of monomers

No. of monomers(n)	HOMO-LUMO	AM1 (eV)	PM3 (eV)	MNDO (eV)
1	18-19	5.78	5.63	5.54
2	32-33	4.91	5.39	5.45
3	49-50	5.15	5.57	5.29
4	67-68	4.03	4.08	4.02
5	83-84	3.99	4.07	4.04
6	100-101	4.65	4.82	4.86

The number of core electrons leads to the reduction of the core-core repulsion between nuclear charges. The exact expression for this term is simply the product of the charges divided by the distance. Here each of the methods AM1, PM3 and MNDO involves at least 12 parameters per atom. The core repulsion for polyaniline with increased chain length has been calculated and is reported in table 4. The core repulsion has been found to increase with the increase in the number of monomers in the chain.

Table 4: Variations in Core repulsion with increasing number of monomers

No of monomers(n)	AM1 (Kev)	PM3 (Kev)	MNDO (Kev)
1	3.2684	3.215	3.291
2	8.4829	8.376	8.433
3	16.377	16.191	16.310
4	27.579	27.220	27.114
5	38.396	37.886	37.757
6	47.750	47.468	47.912

Conclusions

AM1, PM3 and MNDO semi-empirical quantum computational models have been utilized to find variation in the properties of polyaniline with the increase in the number of monomers and it has been observed that the results of AM1 and MNDO are more similar than that of PM3. The study may be further enhanced to study the properties of the other two forms of polyaniline and if the ratio of the three forms are considered in a given ratio.

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