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Theoretical study of the potential energy surface and electric dipole moment of aniline

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ABSTRACT

The potential energy surface (PES) of aniline was comprehensively investigated at different levels in this paper. The stable conformer of aniline has C_S point group while the transition states possess C_S and C_{2V} symmetries. The computed transition states of aniline are highly dependent on the level of the computations including Hartree-Fock, Density functional and Moller–Plesset perturbation theories. The electric dipole moment of the molecule varies by the rotation of the amino group with respect to the phenyl plane, while in the range of 60–120 degrees, the changes of the dipole moment is not noticeable.

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1. Introduction

Aniline is the simplest cyclic compound and aromatic molecule with an amino (NH_2) group. The conformational analysis of the amino group has been of great interest for chemists due to the chemical reactivity of aromatic amines in the past years. Considering the complicated intra-molecular interactions of ring systems due to nuclear dynamics and thermal vibrations in comparison with acyclic compounds, various methods should be investigated to access the geometries and their relative energies. Detailed studies of such systems like aniline might help one to understand the molecular structures, in particular the conformation of the amino group.

This molecule was subject to different experimental [1–5] and theoretical [6–8] studies which have mostly studied its spatial structure. There is a consensus on the non-planarity of aniline, but argues remain on the extent of distortion from the benzene plane.

A Complete geometry optimization of the minimum energy structure and of the transition states for internal rotation and inversion of the amino group using several levels was reported by M. Palafox et al. [9]. Several studies have confirmed its nonplanarity [10,11]. Lister et al. [12], has reported the non-planarity of aniline using microwave spectra. The reported dihedral angle (D) between the amino (NH_2) plane and the benzene plane was about 37.5° [13,14] and X-ray studies by Fukuyo et al. [15] have led to torsion angle of 38° while this molecule was optimized by ab initio calculations by Hehre et al. [16] giving the dihedral angle of 47.7°. Quack et al. [17] and Larsen et al. [18] determined the barriers to inversion and rotation of the amino group in aniline by resonance fluorescence and far-IR spectroscopy. The obtained barriers are 1.5 and 5.7 kcal/mol, respectively.

The use of ab initio methods to study PES of aniline began when Wang et al. published the energy minimum structure and the transition states for internal rotation and inversion of the amino group at Hartree-Fock level. The orientation of the amino group with respect to benzene ring is the most effective parameter on the conformation of this molecule [7]. However, the theoretical and experimental studies of inversion-torsion frequencies in aniline show excellent agreement, which gives a confidence to the calculated potential energy surface [2,19].

Theoretical studies including Catalan et al. [20] and Hehre et al. [16] have employed STO-3G as a minimal basis set rather than split valance diffused and polarized basis sets in order to get better agreement with experimental results. STO-3G and 6-31G overstates the non-planarity of the amino group while basis sets like 4-21G

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understate the non-planarity and the optimized structures are more planar. From this view, a big discrepancy is observed in the results of different basis sets and methods.

Dipole moment is usually used to explain some chemical and physical characteristics of molecules [20] e.g. the total polarity of the system. It shows the rate of the polarity of a polar covalent bond and is a useful quantity to study the intermolecular interactions involving the non-bonded type dipole–dipole interactions. The higher dipole moment causes the strong intermolecular interactions [10]. Small displacement of the atom and simultaneous displacements of several nuclei have an additive effect on the dipole moment changes. In general the larger the dipole change, the stronger the intensity of the band in an IR spectrum [21]. To our knowledge the only gas phase dipole moment study on aniline was done by Lister et al. [12] describing the dependence of molecular dipole moment on the structure of aniline whether it is planar or non-planar.

The objective of this paper is to present a detailed theoretical study of the fully optimized geometries, the conformational potential energy surface (PES) along with electric dipole moment of aniline employing Hartree-Fock, density functional theory [22] (Becke's three parameter hybrid functional combined with Lee–Yang–Parr correlation functional) (B3LYP) [23] and second order Moller–Plesset perturbation theory (MP2), using Dunning's augmented correlation consistent polarized valence basis set of double-ζ quality (aug-cc-pVDZ) and triple-ζ quality (aug-cc-pVTZ) [24–26].

2. Methodology

The geometry of aniline was completely optimized at Hartree-Fock, density functional theory and second order Moller–Plesset perturbation (MP2) levels employing Dunning's augmented correlation consistent polarized valence basis set of double-ζ quality (aug-cc-pVDZ) and triple-ζ quality (aug-cc-pVTZ) basis sets using Gaussian 09 package. No geometrical constraints were imposed to obtain the extrema energy structure of aniline. Three conformers were identified in our optimizations. The first structure which is recognized as the stable conformer has a pyramidal amino group and a plane of symmetry perpendicular to the ring plane (Fig. 1 (a)) which possess C_S point group. The planar structure is the second optimized geometry with C_{2V} point group which is considered as a transition state for the inversion of pyramidal amino group (Fig. 1 (b)). The last optimized geometry is similar to the first one with a 90 degrees rotated amino group around the C1–N bond (Fig 1 (c)). It is obvious that the inversion/rotation of the amino group has significant effect on the computed energy of aniline, so the potential energy surface (PES) is affected by the rotation of this group. The PES of aniline has been explored at the three aforementioned levels, i.e. HF, B3LYP, MP2 exploiting the same basis sets which were used in our optimization. Geometry parameters of molecule including twist angle (γ) which defines the amino group rotation around the C1–N bond have been optimized by keeping the H1–N–C1 and H2–N–C1 angles as constant and imposing a difference of 126 degrees to H1–N–C1–C2 and H2–N–C1–C2 dihedral angles (Fig. 2). It should be mentioned that depending on the level of theory, in the global energy minimum structure (C_S), the difference of H1–N–C1–C2 and H2–N–C1–C2 dihedral angles was ~126 degrees.

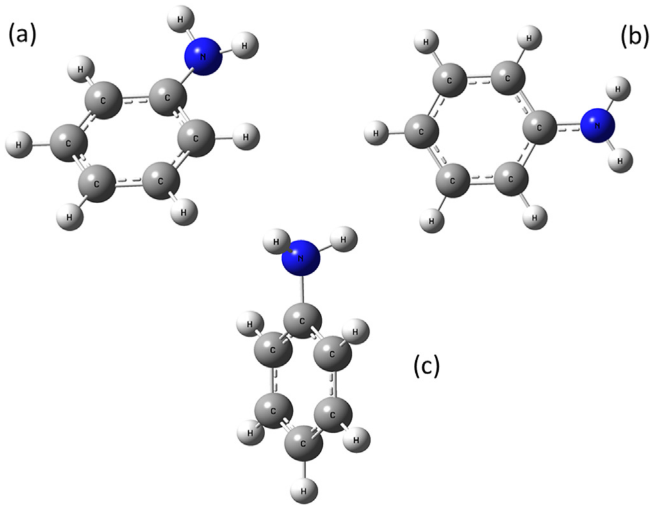

Fig. 1. The predicted conformers of aniline (a) fully optimized global energy minimum structure, (b) the planner transition state structure and (c) transition state structure with a 90 degrees rotated amino group around the C1–N bond.

The potential energy surface was also investigated by folding of the amino plane from −40 to 40. In each step, the H1NH2 angle was scanned in the steps of 1 degree from 105 to 125.

3. Results and discussion

The energies of three conformers of aniline calculated at different levels are presented in Table 1. Table 2 summarizes the optimized structural parameters for the global minimum of the potential energy surface (PES), C_S conformer, using different methods and basis sets. These parameters were compared with experimental [12] and other theoretical [7] data. Approximately no method/basis set dependence is seen in the optimized parameters obtained at different levels.

It is important to determine the amount of the non-planarity of aniline which is mainly caused by amino group [27]. To be more specific, we define the angle (β) between the C1–N bond and H1NH2 plane. As shown in Table 2, this angle varies from 38.7 for B3LYP/aug-cc-pVTZ to 45.4 calculated for mp2/aug-cc-pVDZ. Seemingly B3LYP/aug-cc-pVTZ has the closest value to the measured experimental magnitude. Therefore depending on the method employed the degree of NH_2 pyramidalization (deformation from planarity) changes.

Our results also confirm the former theoretical and experimental studies of aniline implying the pyramidal shape of the amino group. The hydrogen atoms of the amino group are bent out

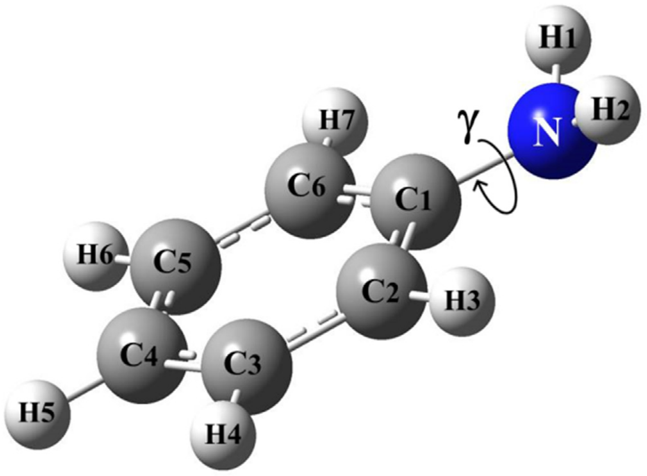

Fig. 2. Aniline geometry: γ defines the amino group rotation around the C1–N bond.

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