



# Molecular structure and solvent effects on the dipole moments and polarizabilities of some aniline derivatives



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## ABSTRACT

This work presents the quantum chemical studies of the effects of substituents and solvents on the ground state molecular geometry, dipole moments, polarizabilities and frontier orbital energies of aniline (A), *N*-methylaniline (NMA), *N*-ethylaniline (NEA), *N,N*-dimethylaniline (DMA) and *N,N*-diethylaniline (DEA) towards understanding their structure–property relationship. The ground state molecular geometry, dipole moments, polarizabilities and frontier orbital energies of A, NMA, NEA, DMA and DEA were computed by use of the ab initio restricted HF–DFT self-consistent field method (B3LYP) with 6-31G<sup>+</sup> basis set in vacuum, ethanol and tetrahydrofuran. The results of the B3LYP/6-31G<sup>+</sup> calculations revealed that these properties are enhanced upon successive substitution with size and number of alkyl groups at the amino group of the molecules, and as the dielectric constant of the solvents decrease. It was also found that for all the molecules, the enhanced ground state molecular geometry, dipole moments and polarizabilities upon substitution or solvent effect are associated with a decrease in the  $E_{\text{HOMO}} - E_{\text{LUMO}}$  (optical) gap. The lower optical gap, higher dipole moments and polarizabilities with increased size and planarity illustrates increased reactivity and ground state electro-optic (non-linear optical) activity of the molecules upon substitution, and as the dielectric constant of the solvents decreased. Of the studied molecules, DEA was found to exhibit the most electro-optic activity and reactivity.

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## 1. Introduction

The conformational preference of chemical substances (especially organic molecules) is an important subject for the understanding of many chemical and biochemical phenomena and reactions involving them [1–3]. As such, molecular conformation is an important aspect of stereochemistry [1]. Subtle changes in the molecular structure of molecules lead to great variations of both physical properties like solubility and stability in ambient air, and optical and electronic properties such as energy gap, electron affinity and electron transfer efficiency; even the stability of the cation(s) or anion(s) produced by such molecules after electron donation or acceptance depends on structural changes at the molecular level [4]. These changes can, for instance, be as a result of a large effect of an environment; a solvent or substituent shell; on the absorption spectrum which changes the electric properties of the molecule(s) [2,5]. For instance, it has been noted that a gradual increase in calculated

molecular properties such as dipole moments and polarizabilities occur with an increase in the dielectric constant,  $\epsilon$ , or polarity of solvents [2,3,6] and the nature of solute–solvent interaction(s) [6]. The solvent, especially polar solvents, could actually affect the geometry as well as molecular properties of molecular systems via long range interactions with the solute molecules thereby stabilizing their frontier molecular orbitals [7]. Thus, in relation to non-polar solvents, polar solvents provide greater solvation energy for the ground state of the solute than the excited state [6].

In substituted anilines, conformational change at low temperature or in suitable solvents affects electronic transition as they are sensitive to the orientation of the amino group due to the interaction of the lone pair of electrons on the group with the  $\pi$ -electrons of the ring which may result in non-radiative processes like inter-system cross-linking [1]. The lone pair electrons give anilines an important chemical reactivity as a base, a nucleophile or an electron donor; in the latter role, anilines have been frequently used in the field of photo-induced electron transfer [8] even though they are weaker bases compared to aliphatic amines because of the electron withdrawing effect of the phenyl group [9]. Therefore, aniline and its derivatives have been widely used as starting materials for chemicals, pharmaceuticals, dyes, electro-optical, biological, materials science and many other industrial processes [1,9–13].

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The conjugated  $\pi$ -electron moiety of these molecules provide a pathway for the redistribution of electronic charge across the entire length of conjugation under the perturbation of an external electric field, and leads to a variation of their electro-optic (EO) susceptibilities. These susceptibilities provide a quantitative measure of the ability of the bulk material to alter its optical properties, and are primarily derived from their molecular structure since they are mainly governed by their chromophores [2]. As such, intramolecular charge transfer (ICT) has been very important in chemistry and biochemistry with the investigation of ICT processes focusing on systems in which donor and acceptor groups are directly connected through a single or  $\pi$ -bond, with the interaction through single bond focused on through-space interaction between the donor and acceptor, and the interaction through  $\pi$ -bond concentrated on orbital overlap between donor and acceptor group(s) [14]. For alkyl substituents, the C–H bonds of the alkyl groups interact with the nearby  $\pi$ -system via hyper-conjugation, while the amino group shares its lone pair electrons with the  $\pi$ -electron cloud in the ring via conjugation whose effect is the donation of electrons from the N–H bond to the ring C–H oscillator [1,11–13].

In the light of the foregoing, experimental dipole moments have been used to estimate the electron distribution in some parts of molecules, and as a rule, the actual moment is usually compared to the anticipated value for a simple structure and the difference interpreted as an electron shift or contribution of a resonance structure [15]. Thus, charge transfer from donor to acceptor group(s) through a single-double bond conjugated path can induce large variations of both the molecular dipole moments and polarizabilities, thereby making IR and Raman activity strong at the same time [12,13]. The efficiency of the charge transfer is reflected in the ground state molecular geometry of molecules. The latter may (in principle) be an indicator of the different electron conjugation effects and hence, a measure of the contribution of the resonance forms to the ground electronic structure of a molecule [16]. More so, studies of natural bond orbitals (NBOs) of molecules [17–19] (especially organic molecules) provide an efficient method for understanding intra- and intermolecular bonding, and interaction among bonds as well as a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. The intra-molecular interaction is usually formed by orbital overlap between bonding and anti-bonding orbitals of a system, and results in the stabilization of such system [17–19].

In recent years, numerous experimental as well as theoretical (DFT) investigations have been performed for the EO or non-linear optical (NLO) properties and other applications of organic molecules. As a result, simple donor–acceptor aromatic derivatives are very much in the area of interest to NLO material science as they are in many respects, good models in checking the workability of modern concepts and computational approaches to provide a better understanding of structure–property relationships. An understanding of the structure–property relations of organic molecules with extended conjugation in turn provides guidelines for the design of novel molecular EO materials. In this regard, quantum chemical investigation has being of great help in the rationalization of experimental results in order to rank the existing molecular structures according to their EO susceptibilities prior to experiment and hence, direct the synthesis of new and promising compounds to organic chemists [1,2,20–25]. As such, quantum chemical studies of simple models such as aniline and its derivatives for the understanding of their electro-optic properties in terms of the influence of structural and solvent effects on such properties would be quite handy. So far, only scanty quantum chemical reports of the variation of ground state frontier orbital energies, dipole moments and polarizabilities of aniline and its

derivatives with geometry and solvents exist. Our work therefore, derives from here and is an attempt to proffer theoretical explanations to the variation of the molecular dipole moments, polarizabilities and frontier orbital energies of aniline (A), *N*-methylaniline (NMA), *N*-ethylaniline (NEA), *N,N*-dimethylaniline (DMA) and *N,N*-diethylaniline (DEA) with molecular geometry and solvents. This, we wish to provide via ab initio Hartree–Fock/density functional theory calculations using the Becke’s three parameter hybrid DFT–Hartree Fock and the Lee–Yang–Parr correlation functional (B3LYP) procedure by means of 6-31G\* basis set as DFT has proved to be extremely useful in treating the ground state electronic and molecular structure of molecules for a good description in recent times [3,17–19,26], thus contributing to knowledge in the domain of experimental and quantum chemical correlations in the understanding and application of aniline and its derivatives. This in the long run, would augment the understanding and development of highly efficient organic EO devices, since the focal point of recent research among many organic materials research groups is towards obtaining organic compounds having delocalized electrons to exhibit extremely large EO responses [20,23,27].

## 2. Computational details

Quantum chemical computations of the ground state molecular geometry, dipole moments, polarizabilities, energies and frontier orbital energies ( $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ ) of aniline, *N*-methylaniline, *N*-ethylaniline, *N,N*-dimethylaniline and *N,N*-diethylaniline were carried out at the ab initio restricted HF–DFT self-consistent field (B3LYP) level of theory [7,12,24] in vacuum, ethanol ( $\epsilon = 24.3$ ) and tetrahydrofuran ( $\epsilon = 7.6$ ) with SPARTAN’10 software package [28] on a 2.10 GHz personal computer. The geometry and energy optimizations of these molecules in the different media leading to the energy minima [3] and determination of the convergence properties of the molecules [9,24] were first performed without any symmetry constraints [7,29] using the analytical gradient methods of B3LYP [3,7,12,13,30,31] by means of the standard polarized basis set; 6-31G\* [4,17,30–35] implemented in the SPARTAN’10 software package [28]. This method has been reported to give results with respect to geometric parameters that show better agreement with experimentally determined values [12,31] compared to the HF and other DFT methods [12], while the basis set permits the molecular wavefunction the flexibility to distort away from the spherical symmetry in the neighborhood of each atom in a molecule thereby augmenting the determination of the degree of distortion or polarization in the molecule [30]. And has therefore, been employed in the calculation of molecular polarizabilities and hyper-polarizabilities [4,17]. All the parameters were then allowed to relax so as to enable all the calculations converge to the optimized geometries of each of the molecules to correspond to an energy minimum obtained by solving the self-consistent field equation iteratively [14,17,18]. The optimized structures were then used to obtain the ground state molecular geometry parameter, dipole moments, polarizabilities, energies and frontier orbital energies ( $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ ) of the studied molecules at the same level of theory (B3LYP/6-31G\*).

### 2.1. Dipole moment ( $\mu$ ) [2,3,7,36–38]

This is the most widely used quantity in describing the polarity of a system. It is the measure of polarity of a polar covalent bond and is defined as the product of charge on the atoms and the distance between the two bonded atoms. The total (static) dipole moment written as;

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (2.1)$$

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