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A comparative study of the infrared and Raman spectra of aniline and o-, m-, p-phenylenediamine isomers

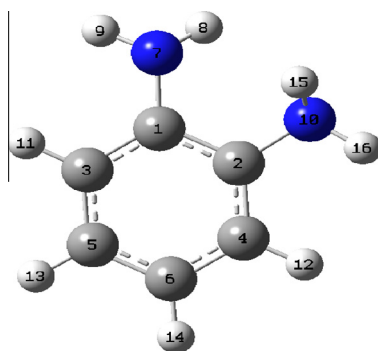
Hassan M. Badawi*, Wolfgang Förner, Shaikh A. Ali

Department of Chemistry, King Fahd University of Petroleum & Minerals (KFUPM), Dhahran 31261, Saudi Arabia

HIGHLIGHTS

- The structures of aniline and phenylenediamines were optimized at the DFT and MP2 levels.
- The vibrational wavenumbers of the molecules were calculated at the DFT level.
- Vibrational assignments were provided by combining experimental and theoretical data.

GRAPHICAL ABSTRACT



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ABSTRACT

The structural stabilities of o-, m- and p-phenylenediamine (PDA) isomers were investigated by DFT-B3LYP and ab initio MP2 calculations with the 6-311G** basis set. From the calculations the three isomers were predicted to exist predominantly in an *anti* (transoid) structure. In the o-isomer, the *syn* (cisoid) form is calculated to turn to the *anti* (transoid) form with the two HNCC torsional angles of about 44 and 10° and the NH₂ inversion barrier of 3–4 kcal/mol. The CCNH torsional angles in the m-PDA and p-PDA isomers were calculated to be about 25–26° as compared to 20° in aniline. A comparison of the Raman spectra of the three PDA-s with those of aniline shows the high sensitivity of the ring breathing mode to the nature of substituents in the aniline ring. The vibrational wavenumbers were computed at the DFT-B3LYP for aniline and the o-, m- and p-PDA isomers for the purpose of comparison. Complete vibrational assignments were made on the basis of normal coordinate analyses and potential energy distributions for aniline and the o-, m- and p-PDA molecules.

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Introduction

The midway structure of aniline (phenylamine) between amines and amides was the subject of theoretical and experimental investigations for some time [1,2]. The conjugation between the amino and phenyl group tends to keep the NH₂ group in the sp² planar structure as in amides, while the steric forces destabilize the planar form and stabilize the sp³ pyramidal structure as in normal amines.

* Corresponding author. Tel.: +966 3 8604208; fax: +966 3 8604277.

E-mail address: hbadawi@kfupm.edu.sa (H.M. Badawi).

The *non-planarity* of the amine nitrogen in aniline was reported to be a result of a balance between two opposing forces: the stabilization by the p-π conjugation of the nitrogen lone pair with the aromatic ring and that gained by the amine moiety using highly directed sp³ orbitals for the bond formation [1]. From a recent study the symmetric *near-planar* structure of aniline was predicted by the DFT-B3LYP, MP2 and MP4(SDQ)/6-311G** levels of theory to be a real minimum on the potential surfaces of the molecule [2]. In the optimized structure the two N–H bonds were predicted to be directed symmetrically towards one side of the benzene ring with a C_s molecular symmetry and an HNCC torsional angle of about 20°. The NH₂ inversion barrier was predicted to be about

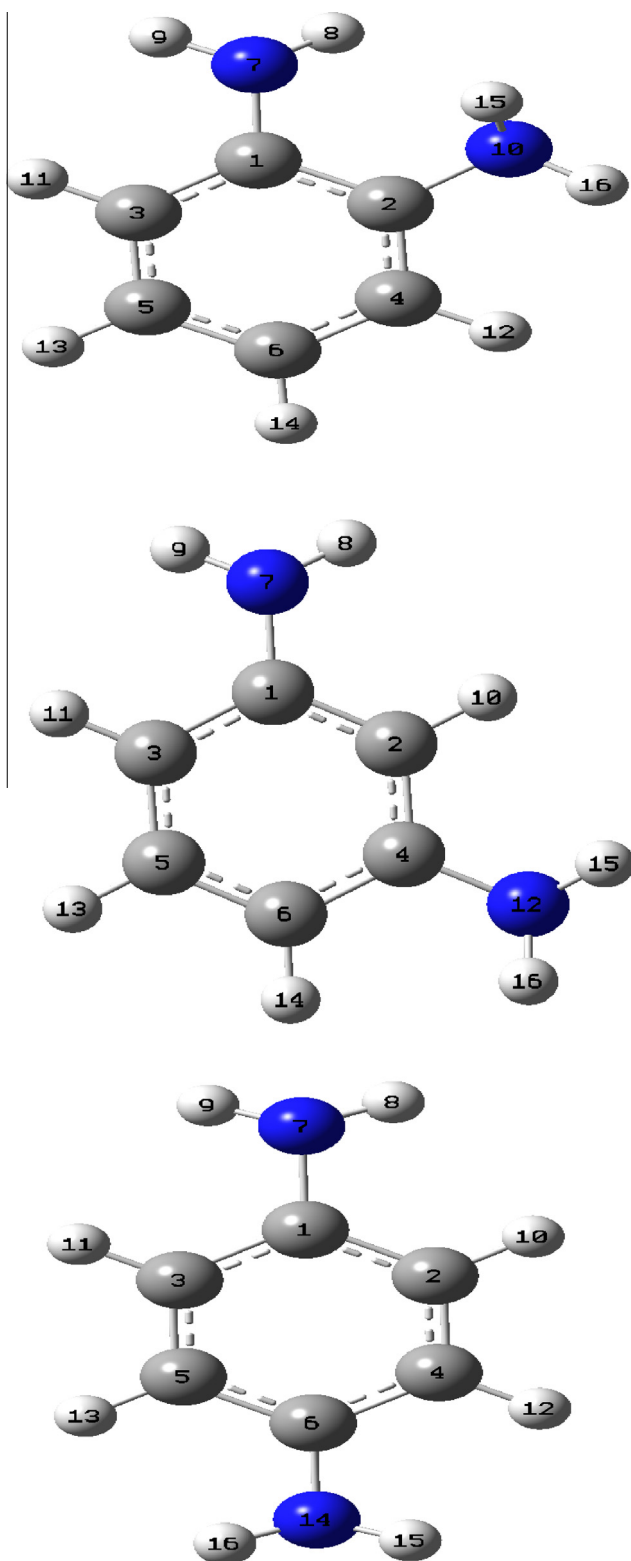


Fig. 1. Atom numbering of the optimized *anti* (*transoid*) structures of o-phenylenediamine (upper), m-phenylenediamine (middle) and p-phenylenediamine (lower).

3.5 and 9.3 kJ/mol at DFT-B3LYP/6-311G** and MP2/6-311G** levels, respectively [2].

The *near-planar* structure was predicted also to be the ground state structure of 2,4,6-trichloro- and 2,3,5,6-tetrachloroanilines. The NH_2 inversion barrier was estimated from the MP2/6-311G**

level of theory to be about 9.6 kJ/mol for aniline, 5.9 kJ/mol for the trichloro and 4.6 kJ/mol for the tetrachloro derivatives. It was reported that the line intensities and the positions of the ring breathing and the C–Cl stretching modes have a strong dependence on the number of chlorine atoms in the benzene ring of aniline [2].

As a continuation of our interest in the structural properties of important anilines, the structures and vibrational spectra of o-, m- and p-phenylenediamines were investigated in the present study. The energies of the three compounds in their possible structures were optimized at the DFT-B3LYP and ab initio MP2 levels of theory using the 6-311G** basis set for the purpose of comparison. The vibrational frequencies were computed for the optimized structures and vibrational assignments were provided on the basis of calculated and experimental data of the molecules. The results of the work are presented herein.

Experimental infrared and Raman spectra

The samples of aniline, o-, m- and p-phenylenediamine (PDA) isomers with about 98% purity were purchased from Fluka Chemical Company. The mid-infrared spectra ($4000\text{--}500\text{ cm}^{-1}$) of the four chemicals were obtained with a Perkin Elmer 16F PC FTIR spectrometer using a NaCl window. The Raman Spectra ($4000\text{--}100\text{ cm}^{-1}$) of the molecules were recorded on a Nicolet 6700 FTIR NXR Raman Module. The atom numbering used for the PDA molecules is shown in Fig. 1. The experimental infrared and Raman spectra of aniline and the three PDA molecules are shown in Figs. 2 and 3.

Ab initio calculations

The GAUSSIAN 03 program [3], running on an IBM RS/6000 43P model 260 workstation, was used to carry out the DFT-B3LYP and MP2 calculations. The 6-311G** basis set was employed to optimize the structures and predict the energies and the dipole moments of o-, m- and p-phenylenediamines in their possible *syn* (*cisoid*) and *anti* (*transoid*) structures (Fig. 1 and S2). The optimized structural parameters of the three molecules are listed in Tables S1 and S2. The optimized relative and total energies of the possible structures of the molecules are given in Table 1 and S1–S2, respectively.

Vibrational frequencies and normal coordinate analysis

The vibrational wavenumbers of aniline and o-, m- and p-phenylenediamines in their *low energy* conformations were calculated at the B3LYP/6-311G** level of theory. Complete assignments of the normal vibrational modes were proposed on the basis of normal coordinate calculations [4] and the calculated infrared band intensities, Raman line activities, depolarization ratios and the experimental infrared and Raman spectra of the four molecules (Tables 2–5). The internal and symmetry coordinates of the aniline molecule are derived from those of the phenylenediamines listed in Tables S3 and S4.

Discussion

The interesting structure [5,6] and biological properties of phenylenediamine (PDA) isomers [7–13] have turned our attention to thoroughly investigate their structural stability and vibrational stability in the present work. The structures of the three isomers of phenylenediamines were previously investigated by MO calculations at the HF and MP2 levels of theory using the 6-31G** basis set [5]. The o-phenylenediamine was reported to exist only in a *transoid* conformer, while the m- and p-isomers to exist in *cis* and *trans* forms. The geometries of the three isomers in chloroform and

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