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FTIR and FTRaman spectroscopic investigation of 2-bromo-4-methylaniline using ab initio HF and DFT calculations

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ABSTRACT

The FTIR and FTRaman spectra of 2-bromo-4-methyl aniline (2-B-4-MA) molecule have been recorded using Brucker IFS 66 V spectrometer in the range of 4000–100 cm^{-1}. The molecular geometry and vibrational frequencies in the ground state are calculated using the Hartree–Fock (HF) and B3LYP with 6-31+G*(d, p), 6-311+G*(d, p) and 6-311++G* (d, p) basis sets. The computed values of frequencies are scaled using a suitable scale factor to yield good coherence with the observed values. The isotropic HF and DFT analysis showed good agreement with experimental observations. Comparison of the fundamental vibrational frequencies with calculated results by HF and B3LYP methods indicates that B3LYP/6-311++G* (d, p) is superior to HF/6-31+G* for molecular vibrational problems. The complete data of this title compound provide the information for future development of substituted aniline. The influences of bromine atom, methyl group and amine group on the geometry of benzene and its normal modes of vibrations have also been discussed.

1. Introduction

Aniline and its substituted derivatives are widely used in a variety of industrial and commercial purposes, including dyestuff, pesticide and pharmaceuticals manufacturing [1]. Some of the para-substituted derivatives of anilines are local anesthetics and the amino group in these molecules plays an important role in the interaction with the receptor. The inclusion of a substitutent group in aniline leads to the variation of charge distribution in the molecule and consequently this greatly affects the structural, electronic and vibrational parameters [2]. Molecular geometry changes due to enhanced interaction between the aromatic ring and the amino group. The planar benzene ring in 2-bromo-4-methyl aniline (2-B-4-MA) has three substitutents, such that the bromine atom and methyl group are at ortho- and para-positions respectively, with respect to the amino group. The methoxy and amino groups are generally referred to as electron donating substitutents in aromatic ring system [3–8]. The amino group in aniline and its derivatives is known to have a pyramidalized geometry resulting from a balance between opposing forces; the stability gained by the molecule as a whole arising from p–π conjugation of the nitrogen lone pair with the aromatic system versus that gained by the amine using highly directed sp^3 orbitals for bond formation. This asymmetric interaction between the amino group and the aromatic ring produces a small displacement of the nitrogen atom out of the benzene ring [9]. Aniline and its derivatives have been subjected to many different types of scientific studies up to now. Several workers [10–20] have studied the spectra of a large number of mono, di, tri and tetra-substituted anilines and related molecules.

More recently [21,22], the experimental vibrational spectra of 3-chloro-4-methyl aniline and 3, 4-dimethoxyaniline have been investigated in comparison with ab initio and DFT values. However, the detailed HF/B3LYP with 6/31+G*(d, p), 6/311+G*(d, p) and 6/311++G*(d, p) basis sets comparative studies on the complete FTIR and FTRaman spectra of 2-bromo-4-methylaniline have not been reported so far. In this study, molecular geometry, optimized parameters and vibrational frequencies are computed and the performance of the computational methods for HF and B3LYP at 6/31+G*(d, p), 6/311+G*(d, p) and 6/311++G*(d, p) basis sets are compared. These methods predict relatively accurate molecular structure and vibrational spectra with moderate computational effort. In particular, for polyatomic molecules the DFT methods lead to the prediction of more accurate molecular structure and vibrational frequencies than the conventional ab initio Hartree–Fock calculations. Among DFT calculation, Becke's three parameter hybrids functional combined with the Lee–Yang–Parr correlation functional (B3LYP) is the best predicting results for molecular

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geometry and vibrational wave numbers for moderately larger molecule [23,24].

2. Experimental details

The compound under investigation namely 2-bromo-4-methylaniline is purchased from Sigma Aldrich Chemicals, U.S.A. which is of spectroscopic grade and hence used for recording the spectra as such without any further purification. The FTIR spectra of the compounds are recorded in Brucker IFS 66 V spectrometer in the range of 4000–100 cm^{-1}. The spectral resolution is ±2 cm^{-1}.

The FTRaman spectra of these compounds are also recorded in the same instrument with FRA 106 Raman module equipped with Nd: YAG laser source operating at 1.064 μm line widths with 200 mW power. The spectra are recorded in the range of 4000–100 cm^{-1} with scanning speed of 30 cm^{-1} min^{-1} of spectral width 2 cm^{-1}. The frequencies of all sharp bands are accurate to ±1 cm^{-1}.

3. Computational methods

The molecular structure of the title compound in the ground state is computed by performing both ab initio HF and DFT/B3LYP with 6-31+G(d, p), 6-311+G*(d, p) and 6-311++G* basis sets. The optimized structural parameters are used in the vibrational frequency calculations at HF and DFT levels. The minimum energy of geometrical structure is obtained using level 6-311+G*(d, p) and 6-311++G *(d, p) basis sets. All the computations have been done by adding polarization function d and diffuse function on heavy atoms [25] and polarization function p and diffuse function on hydrogen atoms [26], in addition to triple split valence basis set (6-311++G*(d, p)), for better treatment of polar bonds of bromine, amino and methyl group. Therefore, we had a discussion on calculated values using these sets. The calculated frequencies are scaled by 0.890 and 0.852 for HF [27]. For B3LYP with 6-31++G(d, p) set is scaled with 0.887, 0.902, 0.911, 930 and 0.942 and 6-311++G(d, p) basis set is scaled with 0.942, 0.952, 0.980, 1.06, and 0.778 [28]. The theoretical results have enabled us to make the detailed assignments of the experimental IR and Raman spectra of the title molecule [29]. HF calculations for 2-bromo-4-methylaniline are performed using GAUSSIAN 03 W program package on Pentium IV processor personal computer without any constraint on the geometry [30–32].

4. Results and discussion

4.1. Molecular geometry

The molecular structure of the 2-bromo-4-methylaniline belongs to C_S point group symmetry. The optimized molecular structure of title molecule is obtained from GAUSSAN 98 W and GAUSSVIEW programs are shown in Fig. 1. The molecule contains bromine atom, amino group and methyl group connected with benzene ring. The structure optimization zero point vibrational energy of the title compound in HF/6-31+G*, B3LYP/6-311+G*(d, p) and B3LYP/6-311++G*(d, p) are −375190.6, −351428.5 and −351101.8 J/mol and 89.67, 83.99 and 83.91 Kcal/mol respectively. The optimized geometries of the title molecule at HF and DFT level theories compared with the experimental geometries of similar molecules 2-chloro-4-methylaniline and 4-bromo benzonitrile [29,33,34] based on X-ray diffraction data. The comparative optimized structural parameters such as bond lengths, bond angles and dihedral angles are presented in Table 1. From the theoretical values, it is found that most of the optimized bond lengths are slightly larger than the experimental values, due to that the theoretical calculations belong to isolated molecules in gaseous phase and the experimental results belong to molecules in solid state [35].

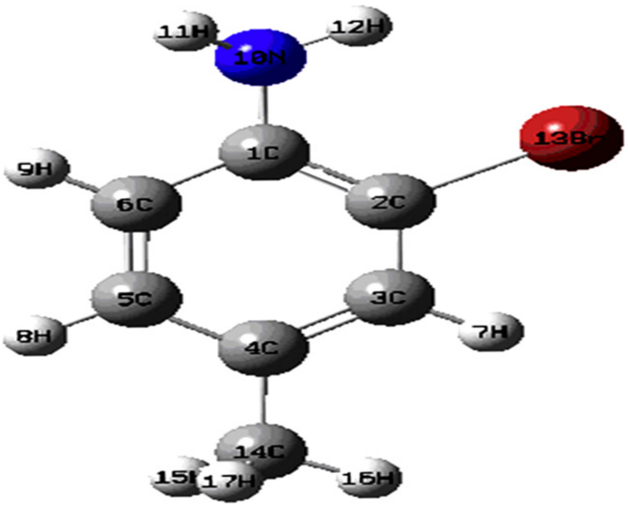

Fig. 1. Molecular structure of 2-bromo-4-methylaniline.

4.1.1. Computed vibrational frequency analysis

The comparative graph of calculated vibrational frequencies by HF and DFT methods at 6-31+G*(d, p), 6-311+G* and 6-311++G*(d, p) basis sets for the title molecule are given in Fig. 2. From the figure, it was found that the calculated (unscaled) frequencies by B3LYP with 6-311++G*(d, p) basis set is closer to the experimental frequencies than HF method with 6-31+G* basis set.

Comparing bond angles and lengths of B3LYP at 6-311++G*(d, p) level with those of HF, as a whole the formers are bigger than later and the B3LYP calculated values correlates well compared with the experimental data. Although the differences, calculated geometrical parameters represent a good approximation and they are the bases for the calculating other parameters, such as vibrational frequencies and thermodynamics properties. The comparative graphs of bond lengths, bond angles and dihedral angles of title molecule for three sets are presented in Figs. 3–5.

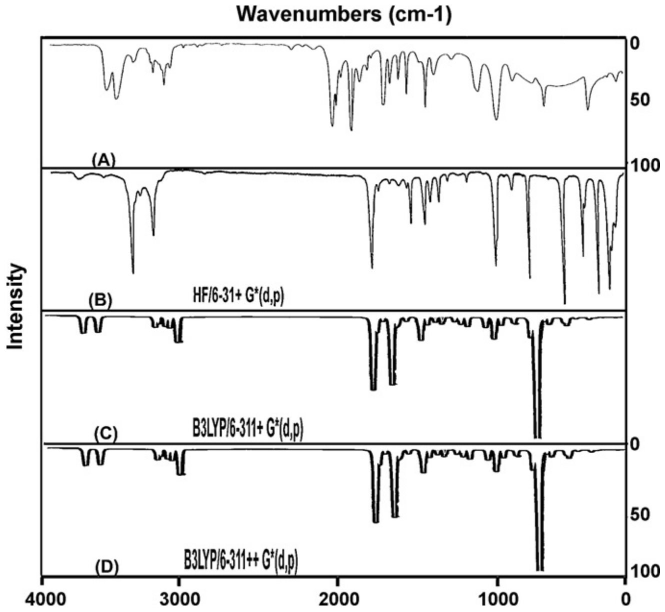

Fig. 2. Comparative graph of experimental and computed frequencies (HF and B3LYP).