



Fourier transform infrared and FT-Raman spectra, assignment, *ab initio*, DFT and normal co-ordinate analysis of 2-chloro-4-methylaniline and 2-chloro-6-methylaniline

V. Arjunan^{a,*}, S. Mohan^b

^a Department of Chemistry, Kanchi Mamunivar Centre for Post-Graduate Studies, Puducherry 605 008, India

^b Centre for Research and Development, PRIST University, Vallam, Thanjavur 613 403, India

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ABSTRACT

The Fourier transform infrared (FTIR) and FT-Raman spectra of 2-chloro-4-methylaniline and 2-chloro-6-methylaniline have been measured in the range 4000–400 and 4000–100 cm⁻¹, respectively. Utilising the observed FTIR and FT-Raman data, a complete vibrational assignment and analysis of the fundamental modes of the compounds were carried out. The vibrational frequency which were determined experimentally are compared with those obtained theoretically from *ab initio* HF and DFT gradient calculations employing the HF/6-31G(d,p) and B3LYP/6-31G(d,p) methods for optimised geometries. The geometries and normal modes of vibration obtained from the HF and DFT methods are in good agreement with the experimental data. The normal co-ordinate analysis was also carried out on the basis of *ab initio* force fields utilising Wilson's FG matrix method. The manifestations of NH– π interactions and the influence of bulky chlorine and methyl group on the vibrational modes of the amino group are investigated.

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1. Introduction

Harmonic force fields of polyatomic molecules play a vital role in the interpretation of vibrational spectra and in the prediction of other vibrational properties. Aniline and its derivatives have been widely used as starting materials in a vast amount of chemicals, pharmaceuticals, dyes, electro-optical and many other industrial processes. The conducting polymer of aniline namely polyaniline is used in microelectronic devices as diodes and transistors [1–4]. The understanding of their structure, molecular properties as well as nature of reaction mechanism they undergo has great importance and has been the subject of many experimental and theoretical studies. A systematic study on the vibrational spectra of simple primary, secondary and tertiary amines received considerable attention in the spectroscopic literature in view of their obvious importance to biological systems and industrial significance. Studies of intermolecular associations, dichroic absorption, band contour of the vapour spectra, measurements of integrated intensities of the absorption bands and theoretical *ab initio* and normal co-ordinate analysis give information regarding the nature of the functional groups, orbital interactions and mixing of skeletal frequencies. Hence, the investigation on the structure and fun-

damental vibrations of aniline and its derivatives are still being carried out, increasingly [5–19]. The inclusion of a substituent in aniline leads to the variation of charge distribution in the molecule, and consequently affects the structural, electronic and vibrational parameters [18]. The electron donating methyl group interacts with nearby π systems through hyper conjugation, while the –NH₂ shares its lone pair electrons with the ring. Both the effects imply electronic delocalisation and are taken into account by the molecular orbital approach [14,17]. The position of the substituents in the benzene ring as well as its electron donor/acceptor capabilities plays a very important role on the structural and electronic properties of the molecules.

The Hartree–Fock (HF) level *ab initio* calculations have been performed to analyse the structural and vibrational characteristics of molecules. However, the use of post-HF level calculations, which include electronic correlation to the calculations, is necessary to get more reliable results on the structural parameters and vibrational properties. Recently, density functional theory (DFT) has been accepted as a popular post-HF approach for the computation of molecular structures, vibrational frequencies and energies of molecules by the *ab initio* quantum chemistry community [20]. Vaschetto et al. [18] showed that the DFT calculations with the hybrid exchange–correlation functional B3LYP (Becke's three parameter (B3) exchange in conjunction with the Lee–Yang–Parr's (LYP) correlation functional) have been proved to be very effective [21,22] for vibrational studies on aniline [23], m-methylaniline

* Corresponding author. Tel.: +91 413 2211111.

E-mail address: varjunftir@yahoo.com (V. Arjunan).

[24] and 4-fluoranyl [15] and show better agreement with the experimental values of structural characteristics of aniline and its derivatives than the calculations containing the gradient corrected exchange functional [25].

Few reports are available on infrared and Raman studies of anilines and its derivatives, but the vibrational spectroscopic analysis of 2-chloro-4-methylaniline and 2-chloro-6-methylaniline has not been carried out. Thus, in the present investigation, owing to the industrial importance of substituted anilines, an exten-

sive spectroscopic studies of 2-chloro-4-methylaniline (2C4MA) and 2-chloro-6-methylaniline (2C6MA) have been undertaken by recording their FTIR and FT-Raman spectra and subjecting them to normal co-ordinate analysis, in an effort to provide possible explanations for the experimentally observed vibrational fundamentals and to understand the effect of halogen and methyl group substitution on the characteristic frequencies of the amino group. In order to obtain the optimised structural parameters, vibrational frequencies, the energy differences among the compounds under study, the

Table 1

Structural parameters calculated for 2-chloro-4-methylaniline (2C4MA) and 2-chloro-6-methylaniline (2C6MA) employing HF/6-31G(d,p) and B3LYP/6-31G(d,p) methods.

Structural parameters	2C4MA		2C6MA	
	HF/6-31G(d,p)	B3LYP/6-31G(d,p)	HF/6-31G(d,p)	B3LYP/6-31G(d,p)
Internuclear distance (Å)				
C1—C2	1.3760	1.3891	1.3820	1.3947
C2—C3	1.3936	1.4019	1.3875	1.3956
C3—C4	1.3817	1.3974	1.3778	1.3921
C4—C5	1.3866	1.3922	1.3837	1.3912
C5—C6	1.3875	1.4054	1.3909	1.4065
C6—C1	1.3979	1.4073	1.4061	1.4171
C5—Cl(8)	1.7519	1.7684	1.7533	1.7697
C6—N7	1.3866	1.3889	1.3875	1.3892
C3—C9	1.5108	1.5106		
C1—C9			1.5101	1.5084
C—H (ring) ^a	1.0760	1.0863	1.0739	1.0853
C—H (methyl) ^a	1.0854	1.0953	1.0858	1.0962
N—H (amino) ^a	0.9947	1.0106	0.9942	1.0100
Bond angle (degree)				
C6—C1—C2	121.4443	121.5104	119.3373	119.3711
C1—C2—C3	121.5628	121.5623	121.8511	121.8129
C2—C3—C4	117.3038	117.4356	119.1313	119.3253
C3—C4—C5	121.1406	120.9290	119.5711	119.3473
C4—C5—C6	121.9172	122.1578	122.1253	122.3329
C5—C6—C1	116.6313	116.4045	117.982	117.8098
C5—C6—N7	122.8170	122.3229	121.9083	121.6711
C1—C6—N7	120.5061	121.2065	120.0564	120.4582
C4—C5—Cl(8)	118.3888	118.8699	118.2187	118.7839
C6—C5—Cl(8)	119.6938	118.9721	119.6561	118.8826
C4—C3—C9	121.5786	121.1754		
C2—C3—C9	121.1175	121.3796		
C6—C1—C9			119.811	119.4010
C2—C1—C9			120.8488	121.2255
C6—C1—H10	118.7020	118.5489		
C2—C1—H10	119.8517	119.9370		
C1—C2—H11	118.8686	118.9378		
C3—C2—H11	119.5686	119.4998		
C3—C4—H12	120.3926	120.3259	121.1377	121.2859
C5—C4—H12	118.4667	118.7449	119.2909	119.3662
C2—C3—H11			120.5820	120.5848
C4—C3—H11			120.2864	120.0897
C1—C2—H10			118.7606	118.5132
C3—C2—H10			119.3872	119.6735
C6—N7—H13	114.6122	115.0707	115.2813	115.6043
C6—N7—H14	115.626	115.3511	115.2813	115.0984
H—N—H (amino) ^a	112.4474	113.0105	112.2178	112.9822
C—C—H (methyl) ^a	111.2608	111.4642	111.2630	111.4967
H—C—H (methyl) ^a	107.6446	107.6214	107.6214	107.3728
Dihedral angle (degree)				
Cl(8)—C5—C4—C3	179.7841	179.6122	179.7338	179.4781
Cl(8)—C5—C6—C1	−179.7805	−179.6305	179.8866	179.6571
Cl(8)—C5—C6—N7	2.6672	3.2975	2.5395	3.1719
N7—C6—C5—C4	−177.5176	176.8749	−177.4742	−177.1182
C5—C6—N7—H13	−155.8984	−156.7723	−150.1603	−152.9471
C5—C6—N7—H14	−22.6196	−22.4102	−16.8125	−18.3138
C1—C6—N7—H13	26.6412	26.2940	32.5464	29.9548
C1—C6—N7—H14	159.9200	160.6561	165.8942	164.5881
C3—C2—C1—H10	179.4657	179.3797		
C4—C3—C2—H11	180.0034	179.8275		
H10—C1—C2—H11	−0.5197	−0.5465		
C4—C3—C2—H10			179.6311	179.8191
C2—C3—C4—H12			179.8962	179.9165
H11—C3—C4—H12			−0.1021	−0.2312

^a Mean value.

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