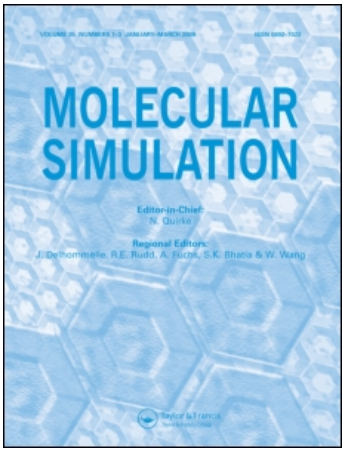

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FT-IR, FT-Raman spectra and DFT vibrational analysis of 2-aminobiphenyl

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FT-IR, FT-Raman spectra and DFT vibrational analysis of 2-aminobiphenyl

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In this work, the Fourier transform infrared (FT-IR) and Fourier transform Raman (FT-Raman) spectra of 2-aminobiphenyl (2ABP) were recorded in the solid phase. The optimised geometry, frequency and intensity of the vibrational bands of 2ABP were obtained by the density functional theory (BLYP and B3LYP) methods with complete relaxation in the potential energy surface using 6-31G(d) basis set. The harmonic vibrational frequencies were calculated and the scaled values have been compared with experimental FT-IR and FT-Raman spectra. The observed and the calculated frequencies are found to be in good agreement. The experimental spectra also coincide satisfactorily with those of theoretically constructed spectrograms.

Keywords: FT-IR and FT-Raman spectra; *ab initio* HF and DFT; 2-aminobiphenyl (2ABP); vibrational analysis

1. Introduction

Biphenyl is used as an intermediate in the production of a variety of compounds (e.g. emulsifier, optical brighteners, crop protection products and plastics), as a heat transfer medium in heating fluids, as a dye stuff carrier of textiles and copying papers, as a solvent in pharmaceutical production and in the preservation of citrus fruits. Aromatic amines are widely used as industrial and laboratory reagents. There is a growing interest in examining quantitative structure activity relationships for the genotoxicity of aromatic amines [1].

There is a satisfactory knowledge of the molecular dynamics of the biphenyl molecule [2,3], symmetrically deuterated biphenyls have been synthesised [4] and the infrared and the Raman spectra have been recorded. The syntheses of most of these compounds have been described in literature [5] but very little is known about their vibrational spectra. A large amount of work has been carried on biphenyl and biphenyl-d_{10} by Katon and Lippincolt [6], Bree [7], Peregudov [8] and Steele and Lippincolt [9]. However, the interpretation of the spectrum does not seem to be completely settled yet. The infrared spectra of some deutero-derivatives have been reported without any comment in a technical report by Scarborough [10]. The molecular configuration of biphenyl in the solid state was first established more than 30 years ago by the observation that the crystals are monoclinic with two molecules in a unit cell of space group $P2_1/\alpha$ [11–13]. This necessitates a molecular centre of symmetry, and hence the two rings must be coplanar. The crystal structure of the biphenyl molecule was investigated by Trotter [14].

To our knowledge, no density functional theory (DFT) calculations and detailed vibrational IR and Raman analysis have been performed on 2-aminobiphenyl (2ABP) molecule. A detailed quantum chemical study will aid understanding of vibrational modes of 2ABP and will clarify the experimental data available for this molecule. DFT calculations are reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity [15–19].

Rauhut and Pulay [20] calculated the vibrational spectra of 31 molecules by using BLYP and B3LYP methods with 6-31G(d) basis set. They reproduced the experimental vibrational frequencies and infrared intensities very well. In their work, they calculated the vibrational frequencies of 20 smaller molecules (the training set), whose experimental vibrational frequencies are well assigned, and derived transferable scaling factors by using the least-square method. The scaling factors are successfully applied to the other 11, larger molecules (the test set). Even when a single scaling factors of 0.995 (0.963) for BLYP(B3LYP) method is employed, root mean square (RMS) deviations for the training and test sets are 26.2 (18.5) and 26.9 (19.7) cm^{-1}, respectively. Thus, vibrational frequencies calculated

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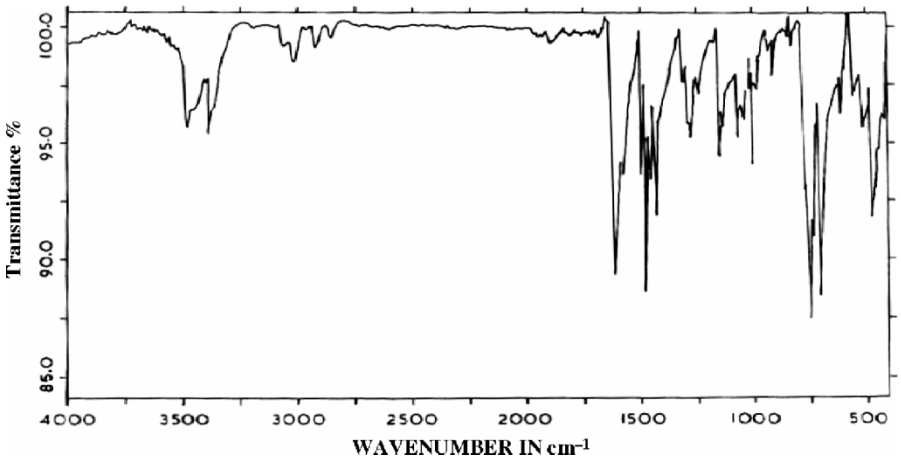

Figure 1. FT-IR spectrum of 2ABP.

by using B3LYP functional with 6-31G(d) basis set can be utilised to eliminate the uncertainties in the fundamental assignments in infrared and Raman vibrational spectra.

In this work, by using DFT (B3LYP and BLYP) methods, we calculate the vibrational frequencies of 2ABP in the ground state to distinguish the fundamentals from the many experimental vibrational frequencies and geometric parameters. These calculations are valuable for providing insight into the vibrational spectrum and molecular parameters.

2. Experimental

The compound 2ABP in the solid form was purchased from Sigma-Aldrich Chemical Company (USA) with a stated purity of greater than 98% and it was used as such without further purification. The Fourier transform Raman (FT-Raman) spectrum of 2ABP has been recorded using 1064 nm line of Nd:YAG laser as excitation wave length in the region 100–3500 cm^{-1} on a Brucker model IFS 66V spectrophotometer equipped with FRA 106 FT-Raman module accessory. The Fourier transform infrared (FT-IR) spectrum of this compound was recorded in the range of 400–4000 cm^{-1} on IFS 66V spectrophotometer using KBr pellet technique. The spectrum was recorded at room temperature, with scanning speed of 30 cm^{-1} min^{-1} and the spectral resolution of 2 cm^{-1}. The observed experimental FT-IR and FT-Raman spectra are shown in Figures 1 and 2. Theoretically predicted IR spectra at B3LYP level of calculations are shown in Figure 3. The spectra have been plotted by employing a Lorentzian peak function taking an average width of 10 cm^{-1}. The spectral measurements were carried out at Sophisticated Analytical Instrumentation Facility, IIT, Chennai.

3. Computational details

All the calculations were performed at Hartree–Fock (HF) and B3LYP levels on a Pentium IV/1.6 GHz personal computer using Gaussian 03W [21] program

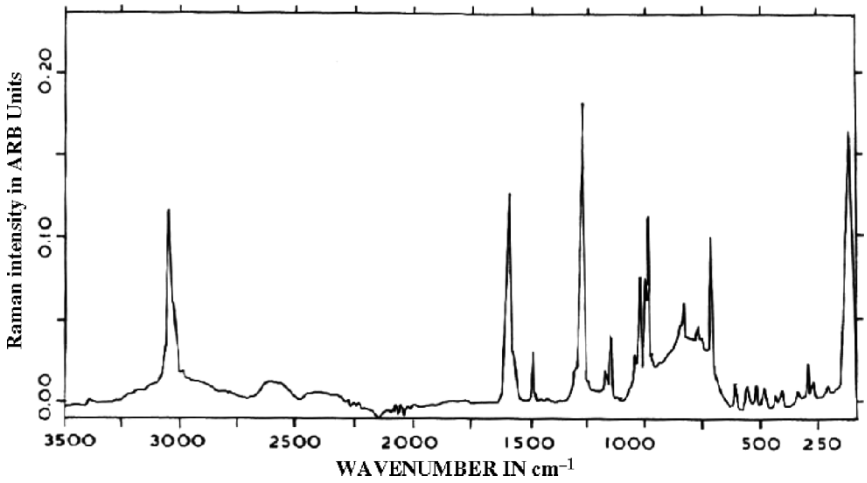

Figure 2. FT-Raman spectrum of 2ABP.

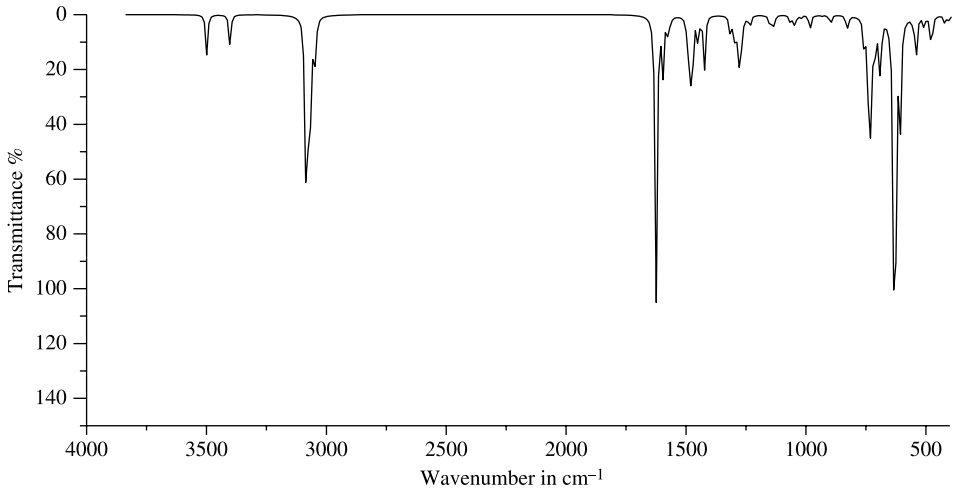

Figure 3. Scaled FT-IR spectrum of 2ABP (B3LYP).

package, invoking gradient geometry optimisation [22]. Initial geometry generated from standard geometrical parameters was minimised without any constraint in the potential energy surface at BLYP level, adopting the standard 6-31G(d) basis set. This geometry was then re-optimised again at B3LYP level, using the same basis set, for better description of polar bonds of amino group. The optimised structural parameters were used in the vibrational frequency calculations at the DFT levels to characterise all stationary points as minima. The 6-31G(d) basis set is employed in the two levels of calculations considered. The smaller basis sets are unreliable and the larger basis sets are expensive. Polarisation functions are necessary to calculate non-planar equilibrium of aniline and its derivatives due to the presence of the amino group's lone pair orbital [23–24]. We have utilised the gradient corrected DFT [25] with the three-parameter hybrid functional (B3) [26] for the exchange part and the Lee–Yang–Parr (LYP) correlation function [27], accepted as a cost-effective approach, for the computation of molecular structure, vibrational frequencies and energies of optimised structures. Vibrational frequencies computed at DFT level have been judged to be more reliable than those obtained by the computationally demanding Moller–Plesset perturbation methods. DFT offers electron correlation frequently comparable to second-order Moller–Plesset theory. Finally, the calculated normal mode vibrational frequencies provide thermodynamic properties also through the principle of statistical mechanics.

By combining the results of the GAUSSVIEW program [28] with symmetry considerations along with available related molecules, vibrational frequency assignments were made with a high degree of accuracy. In order to investigate the performance and vibrational frequencies for the title molecule, mean absolute deviation, standard deviation (SD), RMS value and correlation coefficient (r) between the calculated harmonic and observed fundamental vibrational frequencies for each method and basis set were also calculated and given in Table 4. The RMS values were obtained in this study using the following expression [29].

$$\mathrm{RMS} = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(\upsilon_i^{\mathrm{cal}} - \upsilon_i^{\mathrm{exp}}\right)^2}.$$

These results indicate that the fundamental frequencies calculated (DFT) for the title compound show quite good agreement with experimental values. Furthermore, the 6-31G(d) basis set calculation approximates the observed fundamental frequencies much better than other basis set results. The small difference between experimental and calculated vibrational modes is observed. This discrepancy can come from the formation of intermolecular hydrogen bonding. Also, we note that the experimental results belong to solid phase and the theoretical calculations belong to gaseous phase.

4. Results and discussion

4.1 Molecular geometry

The optimised structure parameters of 2ABP calculated by DFT–BLYP and B3LYP levels with the 6-31G(d) basis set are listed in Table 1, in accordance with the atom numbering scheme in Figure 4. All the geometries determined belong to a true minimum proven by real wavenumbers in the vibrational analysis. As seen from Table 1, a general priority for reproducing the experimental bond lengths taken from [14] is not present among BLYP and B3LYP levels. However, all the interatomic distances computed with the DFT–BLYP

Table 1. Geometrical parameters optimised in 2ABP, bond length (Å), bond angle (°) and dihedral angle (°).

Parameters	BLYP/6-31G(d)	B3LYP/6-31G(d)	Experimental[a] (biphenyl)
Bond length (Å)			
C1—C2	1.432	1.419	1.377
C1—C6	1.416	1.405	1.366
C1—N22	1.410	1.400	–
C2—C3	1.415	1.403	1.425
C2—C11	1.497	1.490	1.507
C3—C4	1.403	1.393	1.370
C3—H7	1.094	1.087	1.100
C4—C5	1.406	1.396	1.382
C4—H8	1.093	1.086	1.060
C5—C6	1.400	1.391	1.406
C5—H9	1.094	1.087	0.970
C6—H10	1.096	1.088	1.140
C11—C12	1.418	1.406	1.377
C11—C13	1.419	1.407	1.360
C12—C14	1.404	1.394	1.425
C12—H15	1.094	1.087	1.100
C13—C16	1.405	1.395	1.406
C13—H17	1.093	1.086	1.140
C14—C18	1.406	1.396	1.370
C14—H19	1.095	1.087	1.100
C16—C18	1.406	1.396	1.382
C16—H20	1.095	1.087	0.970
C18—H21	1.094	1.087	1.060
N22—H23	1.022	1.013	–
N22—H24	1.022	1.013	–
Bond angle (°)			
C2—C1—C6	119.12	119.08	120.7
C2—C1—N22	121.66	121.61	–
C6—C1—N22	119.20	119.29	–
C1—C2—C3	118.18	118.37	118.9
C1—C2—C11	122.41	122.23	121.0
C3—C2—C11	119.40	119.39	120.2
C2—C3—C4	122.31	122.22	120.8
C2—C3—H7	118.05	118.11	118.0
C4—C3—H7	119.63	119.66	121.0
C3—C4—C5	118.99	118.94	118.9
C3—C4—H8	120.26	120.30	118.0
C5—C4—H8	120.75	120.76	121.0
C4—C5—C6	120.12	120.15	119.0
C4—C5—H9	120.42	120.39	121.0
C6—C5—H9	119.46	119.46	120.0
C1—C6—C5	121.28	121.24	120.0
C1—C6—H10	118.75	118.79	118.0
C5—C6—H10	119.98	119.97	120.0
C2—C11—C12	120.19	120.21	120.2
C2—C11—C13	121.98	121.79	120.2
C12—C11—C13	117.80	117.98	118.9
C11—C12—C14	121.18	121.11	120.8
C11—C12—H15	119.02	119.07	118.0
C14—C12—H15	119.80	119.82	121.0
C11—C13—C16	120.96	120.90	120.7
C11—C13—H17	119.33	119.31	127.0
C16—C13—H17	119.69	119.78	112.0
C12—C14—C18	120.27	120.23	120.8
C12—C14—H19	119.64	119.67	118.0
C18—C14—H19	120.09	120.10	121.0
C13—C16—C18	120.41	120.37	120.0
C13—C16—H20	119.53	119.56	120.0
C18—C16—H20	120.06	120.07	118.9
C14—C18—C16	119.38	119.42	120.0

Table 1 – *continued*

Parameters	BLYP/6-31G(d)	B3LYP/6-31G(d)	Experimental[a] (biphenyl)
C14—C18—H21	120.31	120.29	121.0
C16—C18—H21	120.32	120.29	120.0
C1—N22—H23	113.89	113.99	–
C1—N22—H24	114.67	114.77	–
A(23,22,24)	111.50	111.53	–
Dihedral angle (°)			
C6—C1—C2—C3	− 0.52	− 0.53	–
C6—C1—C2—C11	− 179.36	− 179.55	–
N22—C1—C2—C3	− 178.82	− 178.98	–
N22—C1—C2—C11	2.34	2.00	–
C2—C1—C6—C5	0.07	0.11	–
C2—C1—C6—H10	179.91	180.00	–
N22—C1—C6—C5	178.41	178.61	–
N22—C1—C6—H10	− 1.75	− 1.51	–
C2—C1—N22—H23	− 156.18	− 156.32	–
C2—C1—N22—H24	− 26.04	− 25.95	–
C6—C1—N22—H23	25.52	25.22	–
C6—C1—N22—H24	155.66	155.59	–
C1—C2—C3—C4	0.63	0.58	–
C1—C2—C3—H7	179.28	179.36	–
C11—C2—C3—C4	179.50	179.63	–
C11—C2—C3—H7	− 1.84	− 1.59	–
C1—C2—C11—C12	132.85	131.58	–
C1—C2—C11—C13	− 49.10	− 50.29	–
C3—C2—C11—C12	− 45.97	− 47.43	–
C3—C2—C11—C13	132.08	130.70	–
C2—C3—C4—C5	− 0.25	− 0.21	–
C2—C3—C4—H8	179.28	179.36	–
H7—C3—C4—C5	− 178.89	− 178.96	–
H7—C3—C4—H8	0.65	0.61	–
C3—C4—C5—C6	− 0.22	− 0.23	–
C3—C4—C5—H9	− 180.00	179.95	–
H8—C4—C5—C6	− 179.76	− 179.80	–
H8—C4—C5—H9	0.47	0.38	–
C4—C5—C6—C1	0.31	0.27	–
C4—C5—C6—H10	− 179.53	− 179.61	–
H9—C5—C6—C1	− 179.91	− 179.90	–
H9—C5—C6—H10	0.25	0.21	–
C2—C11—C12—C14	177.98	178.03	–
C2—C11—C12—H15	− 2.91	− 2.77	–
C13—C11—C12—C14	− 0.15	− 0.16	–
C13—C11—C12—H15	178.97	179.04	–
C2—C11—C13—C16	− 178.07	− 178.12	–
C2—C11—C13—H17	0.55	0.81	–
C12—C11—C13—C16	0.02	0.04	–
C12—C11—C13—H17	178.64	178.98	–
C11—C12—C14—C18	0.22	0.20	–

[a] Taken from [16].

level of theory are greater than the DFT–B3LYP distances. To the best of our knowledge, experimental data on the geometrical parameters of 2ABP are not available in the literature. Therefore, we could not compare the calculation results given in Table 1 with the experimental data. Only optimised geometrical parameters of 2ABP are compared to those of biphenyl [14]. It has been stated in the literature [30] that HF method underestimates bond lengths and that BLYP methods predict bond lengths which are systematically too long, particularly C—H bond lengths. The B3LYP method leads to geometric parameters which are much closer to experimental data. Because of these reasons we take into account B3LYP/6-31G(d) level for geometric parameters of 2ABP in the present discussion.

The calculated C—C bond lengths in 2ABP molecule are in good agreement with those found in the X-ray structure of biphenyl [14]. For example, in the 2ABP

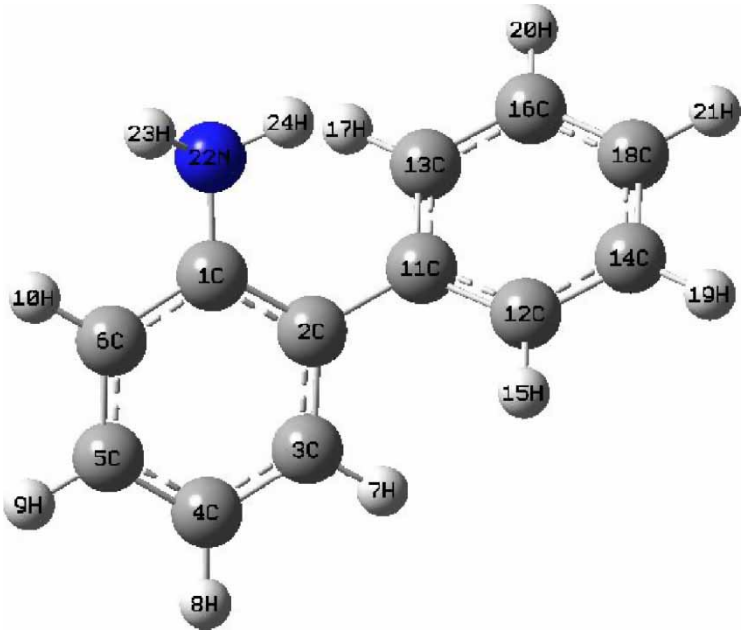

Figure 4. Numbering system adopted in this study (2ABP).

molecule, the first ring C—C bond lengths varies from 1.40 to 1.43 Å by BLYP/6-31G(d) method and 1.39–1.41 Å by B3LYP/6-31G(d) method. For the second ring, the C—C bond lengths varies from 1.40 to 1.42 Å by BLYP/6-31G(d) method and 1.39–1.40 Å by B3LYP/6-31G(d) method.

The benzene ring appears a little distorted with C1—C2 and C1—C6 bond lengths 1.419 and 1.405 Å, respectively, by B3LYP/6-31G(d) exactly at the substitution and rest to the substitution place longer than C3—C4, C4—C5 and C5—C6 bond lengths 1.393, 1.396 and 1.391 Å by the same method. The C2—C1—C6 and C1—C2—C3 angles are calculated as 119, 118° (B3LYP/6-31G(d)) which are smaller than typical hexagonal angle of 120°, respectively. The C2—C3—C4 angle is found to be bigger than the ~2° hexagonal angle. Similar values found to be present in other aniline derivatives which are *o*-methylaniline [31], *m*-methylaniline [32] and *p*-methylaniline [33]. The C1—N bond of *ca.* 1.40 Å by B3LYP method is just 0.03 Å lower than the reported experimental value of 1.43 Å for *p*-methylphenylamine [33].

From the theoretical values, we can find that most of the optimised bond lengths are slightly larger as well as lesser than the experimental values, due to the fact that the calculations have been done on a single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions.

4.2 Vibrational analysis

The molecule of 2ABP consists of 24 atoms, so it has 66 normal vibrational modes. On the basis of a C_s symmetry the 66 fundamental vibrations of 2ABP can be distributed as 21 A″ + 45 A′. The C_s structure was the lowest in energy at all levels. The vibrational bands observed in the infrared region are very sharp, broad and less intense. All these bands have been assigned in terms of various fundamentals, overtone and combination vibrations. Two sets of vibrational frequencies for this molecule are calculated by these methods (BLYP and B3LYP) and then scaled by 0.995 and 0.963 [34], respectively.

4.3 Phenyl ring modes

There are nine CH stretching vibrations observed in both the rings of our compound. The aromatic structure shows the presence of C—H stretching vibrations in the region 3000–3100 cm^{-1} which is the characteristic region for the ready identification of C—H stretching vibrations [35]. There are four C—H bonds observed in the first ring, namely C3—H, C4—H, C5—H and C6—H and five C—H bonds are observed in the second ring, namely C12—H, C13—H, C14—H, C16—H and C18—H. The bands observed at 3069, 3023 and 3009 cm^{-1} in FT-IR and 3055 cm^{-1} in FT-Raman are attributed to C—H stretching vibrations for both the rings, and this is in excellent agreement with the theoretically computed value by B3LYP/6-31G(d) method of frequency range 3093–3051 cm^{-1} (mode nos. 64–56). The strongest Raman line observed at 3055 cm^{-1} corresponds to the symmetric mode of all C—H bonds in the mono-substituted ring one, as in the case of similar compounds [36].

In di-substituted the C—H in-plane bending mode can be expected in the region 1000–1300 cm^{-1}. The bands are sharp but are weak to medium in intensity. The medium and strong intensity bands at 1245, 1175, 1156, 1141, 1070 and 1024 cm^{-1} in FT-IR spectrum are due to in-plane C—H bendings of both rings. The same vibration appears in the FT-Raman spectrum at 1175, 1158 and 1027 cm^{-1} with weak as well as medium intensity. The theoretically scaled values of C—H in-plane bending vibrations also fall in the range 1023–1236 cm^{-1} (mode nos. 33–41) by B3LYP/6-31G(d) method. The absorption bands arising from C—H out-of-plane bending vibrations are usually observed in the region at 675–1000 cm^{-1}. The bands in this region are usually very weak in intensity. The FT-IR bands at 933, 917, 852, 832, 770 and 735 cm^{-1} and FT-Raman band at 773 cm^{-1} are assigned to C—H out-of-plane bending vibration. The theoretically computed values of C—H out-of-plane bending vibration also fall in the region 736–959 cm^{-1} by B3LYP/6-31G(d) method.

4.4 C—C vibrations

The internal stretching of the C—C bonds appears in both the rings at C1—C2, C2—C3, C4—C5, C5—C6 and at C6—C1 for ring one and C11—C12, C12—C14, C14—C18, C18—C16 and C16—C13 for ring two, while C2—C11 make a bridge between the two benzene rings as shown in Figure 4. The internal stretching coordinates of the C—C bonds in 1st and 2nd ring contribute to 12 modes among the 66 listed in Table 2.

The ring carbon–carbon stretching vibrations occur in the region 1625–1430 cm^{-1}. In general, the bands are of variable intensity and are observed at 1625–1590, 1590–1575, 1540–1470, 1465–1430 and 1380–1280 cm^{-1} from the frequency ranges given by Varsanyi [37] for the five bands of 1st and 2nd ring in this region. In the present work, the frequencies observed in the FT-IR spectrum at 1580, 1500, 1480, 1453, 1433 and 1313 cm^{-1} have been assigned to C–C stretching vibrations. The corresponding vibrations appear in the FT-Raman spectrum at 1500 cm^{-1}. The theoretically scaled values at 1599, 1577, 1567, 1495, 1479, 1452, 1426, 1319 and 1296 cm^{-1} shows excellent agreement with experimental data by B3LYP/6-31G(d) method.

The very strong band at 995 cm^{-1} is observed in the FT-Raman spectrum of 2ABP. The corresponding infrared band at 989 cm^{-1} has a weak intensity. These bands arise from the scaled wavenumber at 979 cm^{-1} which can be described as the trigonal ring breathing vibration or the 'star of David' vibration of aromatic ring [38]. The in-plane deformation vibration is at higher frequencies than the out-of-plane vibrations. Shimanouchi et al. [39] gave the frequency data for these vibrations for different benzene derivatives as a result of normal coordinate analysis

The C—C—C out-of-plane bending vibrations of both the ring appear in the standard region 400–790 cm^{-1} [36]. Six modes have the contribution of bending C—C—C coordinates of both rings. The computed value of C—C—C out-of-plane bending vibration by B3LYP/6-31G(d) method shows at (mode nos. 20, 14-11 and 9) 717, 553–477 and 404 cm^{-1} shows very good agreement with experimental observations at 615–479 cm^{-1} in FT-IR and 619–485 cm^{-1} in FT-Raman, respectively.

The C—C—C in-plane bending vibrations observed at 832, 718 and 703 cm^{-1} in FT-IR, 838 and 722 cm^{-1} in FT-Raman shows very good agreement with computed values at 707, 609 and 606 cm^{-1} (mode nos. 19, 16 and 15) by B3LYP/6-31G(d) method.

4.5 Amino group vibrations

The title molecule 2ABP under consideration possesses one NH_2 group. The NH_2 group gives rise to the six internal modes of vibrations as the symmetric stretching (ν_s), the anti-symmetric stretching (ν_{as}), the symmetric planar deformation or scissoring (β_s), the anti-symmetric planar deformation or rocking (β_{as}), the symmetric non-planar deformation or wagging (ω) and the anti-symmetric non-planar deformation or torsion (τ). The symmetric (ν_s) and anti-symmetric (ν_{as}) stretching modes are easily assigned owing to their charecteristic magnitudes in a mono-substituted benzenes. These modes satisfy the following empirical relation, provided the two NH bonds are identical [40].

$$\nu_s = 345.5 + 0.876\,\nu_{as}.$$

In all the primary aromatic amines, the N—H stretching frequency occurs in the region 3300–3500 cm^{-1} [41]. The asymmetric NH_2 stretching vibration is computed at 3505 cm^{-1} by B3LYP/6-31G(d) and 3503 cm^{-1} by BLYP/6-31G(d) method (mode no. 66) shows good agreement with experimental observations at 3471 cm^{-1} in FT-IR spectrum The symmetric stretching vibration is observed at 3386 cm^{-1} in FT-IR and 3380 cm^{-1} FT-Raman shows good agreement with computed value at 3408 cm^{-1} (mode no. 65) by B3LYP/6-31G(d) and 3404 cm^{-1} by BLYP/6-31G(d) methods. Bellamy and Mancy [42,43] suggested that the NH_2 scissoring mode lies in the region 1590–1650 cm^{-1}. We conclude from the above literature value the strong band of 1613 cm^{-1} in FT-IR and very strong band of 1602 cm^{-1} in FT-Raman respectively are assigned to NH_2 scissoring. While the theoretically computed value by B3LYP/6-31G(d) method at (mode no. 55) 1627 cm^{-1} shows very good

Table 2. Experimental, BLYP and B3LYP levels computed vibrational frequencies (cm^{-1}) obtained for 2ABP.

Mode no.	Experimental[a]		BLYP/6-31G(d)		Cal I_{IR}	Cal I_R	B3LYP/6-31G(d)		Cal I_{IR}	Cal I_R	Species	Vibrational assignments[b]
	FT-IR	FT-Raman	Computed	Corrected			Computed	Corrected				
1			61	61	7	0	61	59	1	87	A″	Ring torsion
2			84	84	0	0	88	85	2	81	A″	Ring torsion
3		116 vs	114	114	1	0	116	112	11	130	A″	Ring torsion
4		276 w	202	201	0	1	208	201	4	64	A″	$\gamma C{-}NH_2$
5			269	268	4	0	276	266	39	79	A″	Ring deform
6		299 w	292	291	11	0	300	289	20	50	A″	Ring deform
7		338 w	326	324	2	1	333	321	40	6	A″	NH_2 deform
8			360	358	2	1	361	348	5	2	A′	ρNH_2
9			407	405	0	0	420	404	9	22	A″	γCCC
10		409 w	424	422	22	2	437	421	95	39	A′	$\beta C{-}NH_2$
11	479 s	485 s	481	478	1	5	496	477	54	29	A″	γCCC
12	520 w	522 w	511	509	26	0	528	508	26	2	A″	γCCC
13			544	542	2	1	562	541	19	7	A″	γCCC
14	563 w	560 sh	556	553	2	0	575	553	28	2	A″	γCCC
15			612	609	1	4	629	606	4	2	A′	$\beta CCC + \beta C{-}NH_2$
16			616	612	9	11	633	609	63	18	A′	βCCC
17	615 w	619 w	635	631	11	1	655	631	2	9	A′	ωNH_2
18	703 vs		694	690	11	0	717	691	8	20	A′	βCCC
19	718 w	722 s	710	706	0	1	734	707	1	1	A′	βCCC
20	735 w		718	714	15	0	745	717	1	3	A″	$\gamma CCC + \gamma C{-}H$
21	753 s		736	732	21	0	764	736	1	19	A″	$\gamma CH + \gamma CCC$
22	770 w	773 w	759	755	1	1	787	758	0	4	A″	γCH
23			820	816	3	18	849	818	3	1	A″	γCH
24	832 w	838 w	829	825	22	9	861	830	2	2	A′	βCCC
25	852 w		835	831	24	0	866	834	37	6	A″	γCH
26			892	887	1	2	931	896	6	1	A″	$\gamma CH + \gamma CCC$
27	917 w		902	897	7	190	942	907	50	9	A″	$\gamma CH + \gamma CCC$
28			923	918	5	2	966	930	77	2	A″	γCH
29	933 w		931	926	0	4	973	937	20	0	A″	$\gamma CH + \gamma CCC$
30			954	950	5	11	995	959	16	1	A″	γCH
31	989 w	995 s	985	980	7	0	1017	979	15	5	A′	Ring breathing (ring 2)
32	1007 m	1008 w	992	987	0	0	1023	985	1	4	A′	Trigonal bending (ring 1)
33	1024 m	1027 m	1029	1024	1	0	1062	1023	3	1	A′	$\beta CH + \rho NH_2$
34			1045	1040	0	1	1079	1039	3	1	A′	βCH
35	1040 w	1043 w	1060	1055	4	0	1093	1053	10	4	A′	ρNH_2
36	1070 m		1078	1073	11	0	1111	1069	4	1	A′	βCH
37	1141 m		1146	1141	2	1	1178	1134	9	2	A′	t $NH_2 + \beta CH$
38	1156 m	1158 w	1164	1159	2	1	1193	1149	4	1	A′	βCH
39			1167	1161	0	0	1195	1151	5	3	A′	βCH
40	1175 w	1175 w	1185	1179	22	2	1216	1171	3	5	A′	βCH
41	1245 w		1245	1239	1	5	1284	1236	6	2	A′	βCH
42			1263	1256	26	0	1307	1259	5	1	A′	$\nu C2\text{-}C11$
43	1283 w	1284 s	1289	1282	2	1	1326	1277	1	3	A′	$\nu C{-}NH_2 + \nu CC$

Table 2 – *continued*

Mode no.	Experimental[a]		BLYP/6-31G(d)		Cal I_{IR}	Cal I_R	B3LYP/6-31G(d)		Cal I_{IR}	Cal I_R	Species	Vibrational assignments[b]
	FT-IR	FT-Raman	Computed	Corrected			Computed	Corrected				
44			1312	1306	2	0	1346	1296	1	19	A′	νCC
45	1313 w		1330	1324	1	4	1364	1314	0	4	A′	νCC + t NH_2
46			1338	1332	9	11	1370	1319	3	1	A′	νCC
47	1433 m		1435	1428	11	1	1481	1426	2	2	A′	νCC
48	1453 w		1461	1453	11	0	1508	1452	37	6	A′	νCC
49	1480 s		1488	1480	0	1	1536	1479	6	1	A′	νCC
50	1500 m	1500 w	1500	1492	15	0	1552	1495	50	9	A′	νCC
51			1564	1556	8	0	1627	1567	77	2	A′	νCC
52			1572	1564	1	1	1637	1577	20	0	A′	νCC
53			1594	1586	3	18	1660	1599	16	1	A′	νCC
54	1580 w		1599	1591	12	9	1662	1600	15	5	A′	νCC + δ NH_2
55	1613 s	1602 vs	1640	1632	84	0	1690	1627	104	4	A′	δ NH_2
56	3009 w		3081	3065	1	2	3169	3051	3	1	A′	νCH
57	3023 w		3092	3076	7	190	3179	3062	3	1	A′	ν_{as} CH
58		3055s	3098	3082	5	2	3185	3067	10	4	A′	ν_{as} CH
59			3100	3084	0	4	3187	3069	4	1	A′	ν_{as} CH
60			3106	3091	9	11	3193	3075	9	2	A′	ν_{as} CH
61			3111	3096	3	18	3198	3080	4	1	A′	ν_{as} CH
62			3119	3104	15	9	3206	3087	5	3	A′	ν_{as} CH
63			3124	3108	24	0	3211	3092	3	5	A′	ν_s CH
64	3069 m		3126	3110	1	319	3212	3093	6	343	A′	ν_s CH
65	3386 w	3380 vw	3421	3404	7	190	3539	3408	5	1	A′	ν_s NH_2
66	3471 w		3521	3503	5	2	3640	3505	6	2	A′	ν_{as} NH_2

[a] s, strong; vs, very strong; m, medium; w, weak; vw, very weak; sh, shoulder; [b] ν, stretching; ν_s, sym. stretching; ν_{as}, asym. stretching; β, in-plane-bending; γ, out-of-plane bending; ω, wagging; ρ, rocking; t, twisting; τ, torsion; I_{IR}, IR intensities; I_R, Raman scattering activities.

agreement with experimental observations, compared with BLYP/6-31G(d) method. It is noted that the frequency of scissoring mode of NH_2 group is observed in the vicinity of spectral range of ring stretching modes (8a or 8b) but as always having higher magnitude than these modes. The anti-symmetric (rocking) mode appears in the range $1000-1100\,cm^{-1}$ with variational IR intensity. In the present case this mode is assigned at $1040\,cm^{-1}$ in FT-IR and $1043\,cm^{-1}$ in FT-Raman spectra. The scaled value at $1053\,cm^{-1}$ by B3LYP/6-31G(d) method exactly coincides with experimental observation.

The C—NH_2 stretching vibration are observed as a weak band at $1283\,cm^{-1}$ in FT-IR and $1284\,cm^{-1}$ as a very strong band in FT-Raman shows good agreement with computed value at $1277\,cm^{-1}$ by B3LYP/6-31G(d) method.

The C—NH_2 in-plane bending vibration are observed at $409\,cm^{-1}$ in FT-Raman also shows very good agreement with computed value by B3LYP/6-31G(d) method at $421\,cm^{-1}$. The C—NH_2 out-of-plane bending vibration is observed at $276\,cm^{-1}$ in FT-Raman deviating positively by $\sim 75\,cm^{-1}$ when compared with the B3LYP/6-31G(d) method. As we note that both C—NH_2 in-plane and out-of-plane bending vibration are absent in FT-IR. The NH_2 wagging computed at $631\,cm^{-1}$ (mode no. 17) by B3LYP/6-31G(d) method shows good agreement with experimental spectrum at 615 and $619\,cm^{-1}$ in FT-IR and FT-Raman respectively. The frequency observed at $1141\,cm^{-1}$ in FT-IR are assigned to NH_2 twisting vibration shows deviation of about $\sim 7\,cm^{-1}$ with computed value at $1134\,cm^{-1}$ (mode no. 35) by B3LYP/6-31G(d) method.

5. Other molecular properties

Several calculated thermodynamic parameters are presented in Table 3. Scale factors have been recommended [44] for an accurate prediction in determining the zero-point vibration energies (ZPVE), and the entropy, $S_{vib}(T)$. The variations in the ZPVEs seem to be insignificant. The total energies and the changes in the total entropy of 2ABP at room temperature at different methods also presented.

Table 3. Theoretically computed energies (a.u.), zero-point vibrational energies (kcal mol^{-1}), rotational constants (GHz), entropies (cal $mol^{-1}\,K^{-1}$) and dipole moment (D) for 2ABP.

Parameters	BLYP/6-31G(d)	B3LYP/6-31G(d)
Total energy	−518.4196446	−518.6588885
Zero-point energy	120.91	124.72
Rotational constants	1.8608	1.8896
	0.5187	0.5256
	0.4325	0.4399
Entropy		
Total	100.35	99.25
Translational	41.28	41.28
Rotational	31.00	30.98
Vibrational	28.04	26.99
Dipole moment	1.405	1.345

Table 4. Mean absolute deviation, SD, r and RMS between the calculated and observed fundamental vibrational frequencies of the title compound.

	BLYP/6-31G(d)	B3LYP/6-31G(d)
Mean absolute deviation	7.5000	9.1764
SD	6.8824	6.4419
RMS	10.1792	11.2118
r	0.9999	0.9998

6. Conclusion

The FT-IR and FT-Raman spectra have been recorded and the detailed vibrational assignment is presented for 2ABP for the first time. The harmonic vibrational frequencies, IR intensities, Raman scattering activities and IR spectra of 2ABP were determined and analysed both at DFT–BLYP and B3LYP/6-31G(d) levels of theory. The difference between the corresponding wave numbers (observed and calculated) is very small, for most of fundamentals. Therefore the results presented in this work for 2ABP indicates that this level of theory is reliable for prediction of both infrared and Raman spectra of the title compound. The optimised geometry parameters calculated at BLYP/6-31G(d) are slightly larger than those calculated at B3LYP/6-31G(d) level and the B3LYP calculated values coincide well compared with the experimental data on the whole (Table 4).

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