

Computational Studies on the IR and NMR Spectra of 2-Aminophenol

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Abstract: The geometry of 2-aminophenol has been optimized using HF and DFT methods using two basis sets 6-31 G(d) and cc-pVDZ using Gaussian 03™ software. The optimized geometry has been used for calculating the vibrational frequencies and that has been compared with the experimental values. The H¹ and C¹³ NMR have been calculated by the Gauge Independent Atomic Orbitals (GIAO) method and have been found to be in good agreement with experimental values. The relative molecular orbital energies and shapes have been studied.

Key Words: Aminophenol, IR, NMR, GIAO, and Gaussian 03™.

INTRODUCTION

2-Aminophenol is an organic compound with molecular formula C₆H₄(OH)NH₂. It is an amphoteric molecule and a reducing agent useful for the synthesis of dyes and heterocyclic compounds [1]. 2-Aminophenol can be prepared via the reduction of 2-nitrophenol, and it has a rather high melting point due to internal hydrogen bonding (m.p. 174 °C) [2].

A computational study on the enhanced stabilization of aminophenol derivatives by internal hydrogen bonding has been reported [3]. Jose et al. have conducted the density functional theory (DFT) study on the thermodynamic properties of aminophenols [4]. Experimental and theoretical investigation of first hyperpolarizability in aminophenols have been performed and reported by Franzen et al. [5].

In the present study, the vibrational and NMR spectra of the title compound have been calculated and compared with experimental results [10].

COMPUTATIONAL DETAILS

Calculations of the title compound were carried out with Gaussian 03™ software program [6]. The structure of 2-aminophenol has been optimized at two levels of theory using two basis sets. They are RHF/6-31 G (d), RHF/cc-pVDZ, B3LYP/6-31 G(d) and B3LYP/cc-pVDZ [7, 8]. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. The structural parameters of 2-aminophenol determined by these calculations are listed in Tables 1 and 2 in accordance with the atom numbering scheme in Figure 1.

Tables 1 and 2 compare the calculated bond lengths and angles for 2-aminophenol with those of experimentally available data [10]. Using the optimized geometry, the vibrational frequencies were calculated using the same level of theory and the same basis sets. Harmonic vibrational wavenumbers were calculated using analytic second derivatives to confirm convergence to minima on the potential surface.

Table 1. Bond Lengths(Å) of 2-aminophenol

Atoms	RHF/ 6-31G(d)	RHF/ cc-pVDZ	B3LYP/ 6-31G(d)	B3LYP/ cc-pVDZ
C ₁ - C ₂	1.39	1.39	1.41	1.41
C ₂ - C ₃	1.38	1.39	1.40	1.40
C ₃ - C ₄	1.38	1.39	1.40	1.40
C ₄ - C ₅	1.39	1.39	1.40	1.40
C ₅ - C ₆	1.38	1.38	1.40	1.40
C ₆ - C ₁	1.39	1.39	1.40	1.40
C ₆ - H ₁₅	1.07	1.08	1.09	1.09
C ₅ - H ₁₄	1.08	1.08	1.09	1.09
C ₄ - H ₁₃	1.07	1.08	1.09	1.09
C ₃ - H ₁₀	1.08	1.08	1.09	1.09
C ₂ - H ₁₁	1.43	1.43	1.45	1.45
N ₁₁ - H ₁₂	1.00	1.01	1.02	1.02
N ₁₁ - H ₉	1.00	1.01	1.02	1.02
C ₁ - O ₇	1.34	1.34	1.35	1.35
O ₇ - H ₈	0.95	0.95	0.98	0.98

**Figure 1. Optimized structure of 2- aminophenol**

At the optimized structure (Figure 1) of the examined species, no imaginary wave number modes were obtained, proving that a true minimum on the potential surface was found. The proton NMR and C¹³ NMR of the title compound have been calculated using the gauge independent atomic orbitals (GIAO) method.

Table 2. Bond Angles (°) of 2-aminophenol

Atoms	RHF/ 6-31G(d)	RHF/ cc-pVDZ	B3LYP/ 6-31G(d)	B3LYP/ cc-pVDZ
C ₂ -C ₁ -C ₆	120.2	120.1	120.1	120.0
C ₂ -C ₁ -C ₇	120.5	120.5	119.4	119.2
C ₁ -C ₂ -C ₃	119.2	119.2	119.6	119.7
C ₁ -C ₂ -N ₁₁	116.5	116.5	114.9	114.8
C ₆ -C ₁ -O ₇	119.2	119.4	120.5	120.8
C ₁ -C ₆ -C ₅	119.7	119.8	119.4	119.5
C ₁ -C ₆ -H ₁₅	118.8	118.7	119.0	118.9
C ₁ -O ₇ -H ₈	107.3	106.9	103.9	103.4
C ₃ -C ₂ -N ₁₁	124.2	124.2	125.5	125.5
C ₂ -C ₃ -C ₄	120.9	121.0	120.4	120.4
C ₂ -C ₃ -H ₁₀	119.0	118.9	119.2	119.2
C ₂ -N ₁₁ -H ₉	119.9	111.3	111.4	110.9
C ₂ -N ₁₁ -H ₁₂	119.9	111.3	111.4	110.9
C ₄ -C ₃ -H ₁₀	120.1	120.1	120.4	120.4
C ₃ -C ₄ -C ₅	119.2	119.2	119.5	119.5
C ₃ -C ₄ -H ₁₃	120.3	120.3	120.1	120.2
C ₅ -C ₄ -H ₁₃	120.5	120.5	120.4	120.4
C ₄ -C ₅ -C ₆	120.7	120.7	120.9	120.9
C ₄ -C ₅ -H ₁₄	119.9	120.0	119.8	119.8
C ₆ -C ₅ -H ₁₄	119.4	119.4	119.3	119.3
C ₅ -C ₆ -H ₁₅	121.5	121.5	121.6	121.6
C ₂ -N ₁₁ -H ₁₂	107.8	107.0	107.0	106.0

RESULTS & DISCUSSION

Bond Length

All C-C bond lengths in 2-aminophenol have the same value in both HF and DFT methods. The C-H bond length exhibits slight variations when basis set changes from 6-31G (d) to cc-pVDZ in the Hartree-Fock (HF) method. The same bond length has unaltered values in the DFT method. N-H bond length has the same values in DFT method for both basis sets, whereas in HF method bond length increases by 0.01Å as the basis set changes from

6-31G(d) to cc-pVDZ. C=O bond length has same values in the HF and DFT methods. The C=O bond length increases by 0.01Å as the theory changes from RHF to DFT. O-H bond length has same values in HF and DFT method as basis set varies from 6-31G(d) to cc-pVDZ. O-H bond length increases by 0.03Å as theory changes from RHF to DFT. The bond lengths of 2-amino phenol are given in Table 1.

Bond Angles

In 2-aminophenol the bond angle values obtained by RHF and B3LYP calculations exhibit a slight difference in 6-31G(d) and cc-pVDZ basis sets. But in some cases, like C₁-C₂-N₁₁, C₁-O₇-H₈, C₆-C₁-O₇, C₄-C₅-H₁₄, there is much

difference in bond angles of RHF and B3LYP calculations. The bond angles of 2-amino phenol are given in Table 2.

Vibrational Frequencies

The vibrational frequencies were calculated computationally using two basis sets 6-31G(d) and cc-pVDZ and two theories RHF and B3LYP. The DFT hybrid B3LYP tends to overestimate the fundamental modes, therefore scaling factors have to be used for obtaining a considerably better agreement with

experimental data. Therefore, a scaling factor of 0.9613 and 0.8929 was uniformly applied to the wavenumbers calculated using DFT and HF, as suggested in Gaussian 03™ [9]. The vibrational frequency obtained from the calculation using RHF method was multiplied by a factor 0.8929 and by 0.9613 in DFT method for scaling. The frequencies are then being compared with the experimental spectrum obtained from the SDBS website [10]. The computational and experimental frequencies of 2-aminophenol with their assignments are given in Table 3 [11, 12].

Table 3. Infra Red Vibrational Frequencies(cm⁻¹) and their assignments

Modes of Vibration	RHF/ 6-31G(d)	RHF/ cc-pVDZ	B3LYP/ 6-31G(d)	B3LYP/ cc-pVDZ
N-H assym.stretching	3412	3386	3404	3390
O-H stretching	3378	3620	3584	3393
C-H sym. stretching	3093	3013	3031	3080
C-H assym. stretching	3082	3004	3021	3072
C-H assym. stretching	3064	2985	3003	3054
C-H assym. stretching	3051	2973	2990	3041
N-H bending	1626	1608	1636	1642

H¹ NMR

The proton NMR of the title compound has been calculated using the gauge independent atomic orbitals (GIAO) method [13, 14]. From the isotropic values of the molecule and that of TMS we obtain the δ values of the nmr spectrum. The isotropic value of the protons of TMS

is 31.6198 in the RHF calculation and 31.7825 in B3LYP calculation. The proton-nmr spectrum of 2-aminophenol is taken from the website SDBS [10]. The δ values of 2-aminophenol are given in Table 4.

Table 4. δ values of H¹ NMR of 2-aminophenol

Proton	RHF/ 6-31G(d)	RHF/ cc-pVDZ	B3LYP/ 6-31G(d)	B3LYP/ cc-pVDZ	Exeperimental Value [10]
8	4.5343	5.4842	6.9493	7.4618	8.9
9 & 12	0.0959	1.2265	1.2968	1.9253	4.4
	0.0952	1.2272	1.2977	1.9262	4.4
15	5.9322	7.0589	6.6391	7.0936	6.587
10	5.4016	6.5323	6.2952	6.7283	6.543
13	6.0264	7.1094	6.7479	7.1718	6.649
14	5.670	6.7859	6.4479	6.8969	6.400

The proton-nmr spectrum of 2-aminophenol exhibits six peaks. This indicates six types of protons. The computationally calculated values of protons 8, 9, 12, 10,

15, 13 and 14 agree with the experimental values, but the computationally calculated values of protons 9 and 12 are less than the experimental values in both HF and DFT

methods. The chemical shift values calculated by GIAO method show slight difference from the experimental values, but maintain a general trend of chemical shift.

C¹³ NMR

The isotropic value of the C¹³ of TMS is 195.1196 in the RHF theory and 188.7879 in the theory B3LYP. The C¹³ nmr spectrum of the molecule is taken from the

website SDBS [10]. From the isotropic values of the carbon of 2-aminophenol and the TMS we obtain the δ values of their C¹³ nmr spectrum. The δ values of 2-aminophenol are given in Table 5. The C¹³ spectrum of 2-aminophenol reveals 6 peaks, which indicates 6 different types of carbon atoms. From the computational calculations also we have 6 values which agree with the experimental values.

Table 5. δ values of C¹³NMR of 2-aminophenol

C ¹³ type	RHF/ 6-31G(d)	RHF/ cc-pVDZ	B3LYP/ 6-31G(d)	B3LYP/ cc-pVDZ	Exeperimental Value [10]
1	146.123	149.46	151.84	143.13	143.95
2	114.21	117.84	122.64	111.51	116.48
3	123.22	125.91	123.52	119.58	136.40
4	107.86	110.04	112.48	103.71	114.47
5	122.64	125.12	123.65	118.79	119.47
6	106.04	107.86	109.13	101.53	114.44

HOMO-LUMO energy gaps

The relative energy of the molecular orbitals have been calculated and a graphical representation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of 2-aminophenol are given in Figures 2(a) and (b).

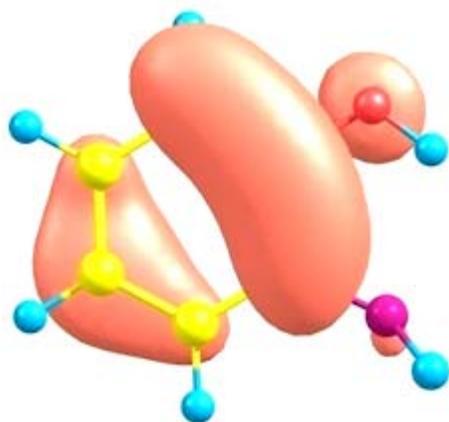


Figure 2(a). HOMO of 2-aminophenol

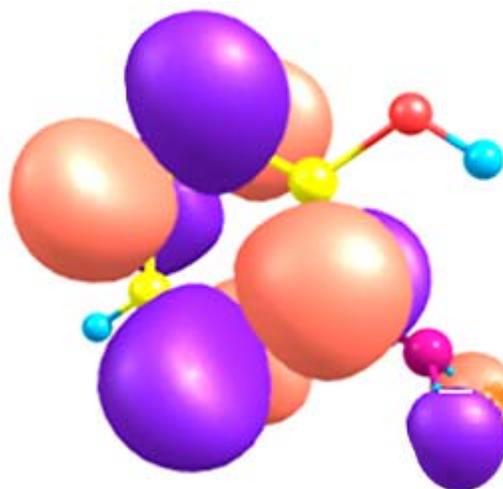


Figure 2(b). LUMO of 2-aminophenol

CONCLUSION

The structure of 2-aminophenol was optimized by the RHF and DFT methods using the basis sets 6-31 G (d) and cc-pVDZ. Using the optimized geometry, the vibrational frequencies, proton NMR and C¹³ NMR of the title compound have been calculated and have been

found to agree well with experimentally reported values. The small differences are due to the fact that experimental values are recorded in the solid state and theoretical calculations belong to the gaseous phase. A plot of the highest occupied molecular orbital (HOMO) and that of the lowest unoccupied molecular orbital (LUMO) is also made.

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