



Synthesis and vibrational study of 2-amino, 3-chloro 1,4-naphthoquinone by DFT

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Abstract : 2-amino,3-chloro 1,4-naphthoquinone was synthesized. The Vibrational wave numbers of this compound have been calculated using Gaussian 09 software code, employing Density Functional Theory. The IR data is compared with experimental values. The predicted infrared intensities and Raman activities are reported. The calculated frequencies are in good agreement with the experimental values. The calculated geometrical parameters are also given. The study is extended to calculate the HOMO-LUMO energy gap, Ionization potential (I), Electron affinity (A), Global hardness (η), chemical potential (μ) and global electrophilicity (ω). The calculated HOMO-LUMO energies show the charge transfer occurs in the molecule. Optimized geometrical parameters of the title compound are in agreement with similar reported structures.

Keywords : 2-amino,3-chloro 1,4-naphthoquinone, IR, DFT, Energy gap.

1. Introduction

The quinonoid structure was widespread in nature and the quinones encompass over 1200 naturally occurring compounds (1). Naturally occurring quinones have several different roles in organisms; they were functional constituents of several biochemical systems (e.g. ubiquinone and vitamin K they are dyes, or they act as defensive compounds. Quinones found use as pharmaceuticals (e.g. the anthracyclinecytostatics) and they were environmental pollutants (2). The exposure of cells to quinonoid compounds might lead to several deleterious consequences. Chronic exposure to quinones might be carcinogenic; several quinones are mutagenic in the Ames test (3, 4), as well as to cultures of eucaryotic cells (5).

The electrophilicity, on the other hand, was mainly determined by the electron density at the carbons in the quinonoid double bond ($C_2=C_3$). In studies of cell toxicity it has to be considered that a quinone that formed a stable hydroquinone will be hindered from electrophilic addition by reduction because the hydroquinone was not an electrophile. The capacity to produce free radicals was dramatically influenced by the substituent's present on the quinonoid molecule. The unsubstituted 1, 4-naphthoquinone had an E_7' value that allows rather efficient one-electron reduction(6).

1,4-Naphthoquinones, possessing an amino or a substituted amino group in the 2-position, have been a subject of study for many years because of their use in a variety of medical and biological applications, including as antituberculars, antimalarials, antibacterials, antitumor agents, larvicides and molluscicides, herbicides, and fungicides [7-11] The introduction of amino substituents onto the quinonemoeity can exert influence on its redox properties, inducing oxidative stress in cells and alkylation of DNA. The aminoquinones

are found in important bioactive compounds such as antimalarial agents (12). This paper describes synthesis and vibrational spectra of 2-amino,3-chloro 1,4-naphthoquinone calculated by DFT basis set, the data is compared with experimental values. The wave number values computed by the HF method and 6-31 G* level contain known systematic errors due to negligence of electron correlation (13). We therefore have used the scaling factor as 0.90 for HF/6-31G* set. Geometrical parameters, Mulliken atomic charges and HOMO – LUMO energy gap of the chelate is reported.

2. Materials and Methods

Synthesis of 2-amino,3-chloro 1,4-naphthoquinone was carried out as per the procedure given by Matsura Makoto et al.(14). The reaction between methyl amine in methanol with 2,3- dichloride -1, 4- naphthoquinone over 2hr at 30-40 °C and the yield was 96.6 %.

2.1 Instrumental Analysis

Elemental analysis was carried out with a Perkin Elmer 2400 series for C, H, and O & N. The IR spectra were recorded on a JASCO FTIR spectrophotometer model in a KBr matrix and in the range of 4000 – 400 cm⁻¹.

2.2.1 Computational details

The entire calculations conducted in the present work were performed DFT method and frequency-RB3LYP with LANL2DZ basis set in the Gaussian 09 software code. The geometries were first determined at the Density functional theory level of employing SDD basis set (15,16). The wave number value computed theoretically contains known systematic error due to the negligence of electron correlation. We have used the scaling factor value of 0.9393 for HF /SDD basic set. The absence of imaginary wave number on the calculated Vibrating Spectrum confirms that the structure corresponds to minimum energy. HOMO-LUMO energy gap and other related molecular parameters are calculated.

3. Results and Discussion

About 45 infra-red bands in the 2-amino,3-chloro 1,4-naphthoquinone have been observed in the calculation by DFT method. The wave numbers of all the calculated and observed frequencies are given in Table 1. The probable modes of vibrations assigned for the observed frequencies are given in the last column of the table. The assignments of the fundamental frequencies made on the basis of intensity considerations and position of observed frequencies.

Table 1 : IR frequencies calculated and observed wave numbers of 2-amino,3-chloro 1,4-naphthoquinone

Sr. No.	Frequency cal. cm ⁻¹	In. cal. km / mol	Raman Activity -A ⁴	Obd. cm ⁻¹	In. Ob. % T	ASSIGNMENTS
1	32.00	0.26	0.92	--	--	C-H Bending o.p.
2	58.49	0.80	0.25	--	--	C-H Bending o.p
3	113.68	1.04	2.07	--	--	C-Cl Bending
4	214.40	0.34	2.22	--	--	C-H Bending o.p
5	218.10	6.01	3.13	--	--	C-Cl Bending
6	279.99	9.98	2.88	--	--	N-H Bending
7	307.12	2353	1.93	--	--	C-N Bending
8	373.28	20.28	3.36	--	--	C-Cl Stretching
9	404.86	26.74	1.92	--	--	C-N Bending
10	406.46	3.59	0.37	--	--	C=O Bending
11	418.31	3.62	0.63	--	--	C-H Bending o.p.
12	439.53	3.20	2.82	462.83	45.44	C-N Stretching
13	514.57	4.35	44.07	--	--	Deformation
14	529.66	9.08	1.65	529.36	53.63	Deformation
15	585.34	38.27	3.89	599.75	66.50	C-H Bending o.p.
16	640.94	232.28	9.10	--	--	N-H Bending

17	679.67	33.75	8.85	--	--	N-H Bending
18	685.39	35.53	3.55	--	--	C-H Bending o.p
19	695.93	14.90	1.44	719.31	48.30	C-H Bending o.p
20	733.60	30.89	4.05	--	--	C-H Bending o.p
21	777.16	23.31	1.18	822.49	68.35	C=O Bending
22	852.87	2.51	1.73	852.38	58.32	C-H Bending o.p
23	877.10	84.09	12.50	--	--	
24	911.13	1.65	0.91	--	--	C=O Stretching
25	944.56	3.37	0.79	968.09	79.50	Deformation
26	998.46	3.55	0.24	--	--	C-H Bending o.p
27	1015.82	0.00	0.10	1003.77	72.05	C-H Bending o.p
28	1025.77	32.09	14.93	1037.52	80.60	C-N Stretching
29	1062.94	5.43	33.63	--	--	C-H Bending I.P.
30	1123.33	3.63	4.06	1105.01	77.42	N-H Bending I.P.
31	1133.74	24.87	8.47	--	--	N-H Bending I.P.
32	1182.02	1.51	0.60	1165.76	82.43	C-H Bending I.P.
33	1245.82	38.32	38.69	1228.43	80.18	C-H Bending I.P.
34	1267.87	4.94	4.08	1275.68	58.87	C-NScreeching
35	1320.70	17.84	3.23	1334.50	67.53	C-NScreeching
36	1430.17	10.83	12.56	1390.42	56.26	C=C Screeching
37	1455.81	4.99	49.28	1455.99	83.61	C-H Bending I.P.
38	1466.31	10.66	29.18	--	--	C-H Bending I.P.
39	1541.63	99.87	14.01	1559.17	58.23	C=C Screeching
40	1599.86	88.61	13.11	1604.48	62.85	C=C Screeching
41	1640.84	12.79	268.48	--	--	C=O Screeching
42	1643.93	108.66	34.02	--	--	N-H Bending
43	1666.20	176.66	66.41	--	--	C=O Screeching
44	1676.41	300.00	52.32	1686.44	55.29	C=O Screeching
45	1716.63	111.48	117.48	1864.83	86.44	C=C Screeching
46	1725.92	105.75	220.33	1985.36	86.16	C=O Screeching
47	3361.58	4.50	41.99	3113.51	79.38	v (C-H)
48	3375.00	3.74	62.19	3325.64	71.06	v (C-H)
49	3384.55	0.21	34.13	3415.31	64.74	v (C-H)
50	3395.40	19.96	219.90	3532.95	86.16	v (C-H).
51	3752.93	34.09	183.41	3793.30	77.65	N-H Bending I.P.
52	3868.39	19.43	56.97	3870.22	70.54	N-H Bending I.P.

C--H stretching frequencies

v (C-H) of this ligand frequencies are predicted at 3361.58 3375.00 3384.55 and 3395.40 cm^{-1} by DFT theory. The observed frequencies are at 3113.51, 3325.64, 3415.31 and 3532.95 cm^{-1} respectively.

C—C stretching frequencies

The C—C stretching vibrations of this compound are in the region 1357 – 1650 cm^{-1} for 2-amino,3-chloro 1,4-naphthoquinone. The predicted frequencies are at 1430.17, 1541.56 And 1599.86 cm^{-1} and the observed frequencies in recording IR spectrum are at 1390.42, 1599.17 and 1604.48 cm^{-1} . which have been taken as totally symmetric a_1 type of vibrations. In addition to these, the vibration at 1466.31 m^{-1} have been taken as such, corresponding to 1460 cm^{-1} (a_{ge}) of naphthalene.

C—N stretching frequencies

In nitrosophthoquinone compounds nitrogen is directly attached to the ring and the stretching vibration of the phenyl carbon nitrogen bond is expected in the range of 1330 -1260 cm^{-1} (17, 18). We observed

this ν CN mode at 1267.87 and 1320.70 cm^{-1} in IR and 1275.68 and 1334.50 cm^{-1} in DFT calculations. Akalin and Akyuz (19) assigned C-N stretching at 1268 cm^{-1} in the Raman spectrum for paraphenylenediamine.

C- Substituted vibrations :

C=O group frequencies, in the stretching region of the infra red spectra of 2-amino,3-chloro 1,4-naphthoquinone are predicted at 911.33, 1640.84, 1666.20, 1676.41 and 1725.92 cm^{-1} while only two bands have been observed at 1686.44 and 1985.36 cm^{-1} .

C=O group frequencies, in the bending region of the infra red spectra of 2-amino,3-chloro 1,4-naphthoquinone are predicted at 406.46 and 777.16 cm^{-1} while only one band have been observed at 822.29 cm^{-1}

The C-H bending out of plane vibrations

The C-H bending out of plane vibrations are predicted at 423, 424, 515, 516, 669, 670, 727, 728, 793, 795, 820, 825, 951 and 953 cm^{-1} for 2-amino,3-chloro 1,4-naphthoquinone and we observed bands at 1165.76, 1228.43 and 1445.99 cm^{-1} .

C-H in plane bending vibrations

The C-H in plane bending vibrations are predicted at 32.0, 58.49, 214.4, 418.37, 585.34, 685.39, 695.93, 733.6, 822.87, 998.46 and 1015.82 cm^{-1} for 2-amino,3-chloro 1,4-naphthoquinone and we found only one band at 719.31 cm^{-1} .



Fig. 1 Molecular structure of 2-amino,3-chloro 1,4-naphthoquinone

Molecular geometry.

The optimized structure parameters of 2-amino,3-chloro 1,4-naphthoquinone calculated by ab initio, DFT basis set are listed in Table 2 in accordance with the atom numbering scheme given in Fig -1. The values of bond length in Å , and bond angles in degree are given in Table 2.

Table No:-2 Bond Length and Bong Angle of 2-amino,3-chloro 1,4-naphthoquinone

Bond	Bond Length Å^0	Bong Angle	($^{\circ}$)
C1C2	1.4014	C4C9O15	120.00
C2C3	1.4014	O15C9C12	120.00
C3C4	1.4014	C9H12N18	120.00
C4C5	1.4014	H20N18C12	109.47
C5C6	1.4014	H19N18C12	109.47
C4C9	1.4014	C12C13Cl 17	120.00
C3C8	1.4014	C117C13C8	120.00
C9C12	1.4014	-	-
C12C13	1.4014	-	-
C8O14	1.2584	-	-
C9O15	1.2584	-	-
C13Cl7	1.76	-	-

C12N18	1.47	-	-
N18H19	1.00	-	-
N18H20	1.00	-	-

Mulliken charges arise from the Mulliken population analysis (20,21) and provide a means of estimating partial atomic charges from calculations carried out by the methods of computational chemistry, particularly those based on the linear combination of atomic orbital's molecular orbital method, and are routinely used as variables in linear regression QSAR procedures(22). In the application of quantum mechanical calculation to molecular system, the calculation of effective atomic charges plays an important role. The electron distribution of 2-amino,3-chloro 1,4-naphthoquinone is compared in the two different mechanical methods and the sensitivity of the calculated charges to change in choice of methods is studied. By determining electron population of each atom in the defined basis function, the Mulliken charges are calculated by DFT/SDD. The results are presented in Table-3 which the values of atomic charges of each atom of the concerned molecule (23).

Table-3:- Mulliken Atomic Charges of 2-amino,3-chloro 1,4-naphthoquinone

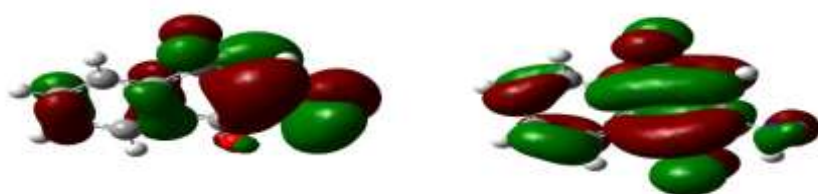
Sr. No.	Atom	Atomic charge
1	1C	-0.213431
2	2C	-0.357893
3	3C	0.330173
4	4C	0.375096
5	5C	-0.362244
6	6C	-0.216718
7	7H	0.245984
8	8C	0.087814
9	9C	-0.11939
10	10H	0.296527
11	11H	0.245023
12	12C	0.297547
13	13C	-0.54316
14	14C	-0.22125
15	15O	-0.241295
16	16H	0.298962
17	17Cl	0.068940
18	18N	-0.583513
19	19H	0.303987
20	20H	0.308851

HOMO-LUMO energy gap and related molecular properties.

The HOMO-LUMO energy gap of the molecule 2-amino,3-chloro 1,4-naphthoquinone in the DFT and SDD basis set has been calculated. The HOMO-LUMO energy gap is constant in both methods. It is known that the value of E_{HOMO} is often associated with the electron donating ability of inhibitor molecule, higher values of E_{HOMO} is an indication of the greater ease of donating electrons to the unoccupied orbital of the receptor. The value of E_{LUMO} is related to the ability of the molecule to accept electrons, lower values of E_{LUMO} shows the receptor would accept electrons. Consequently, the value of Energy gap provides a measure for the stability of the formed complex on the metal surface. The framework of SCF MO theory, the ionization energy and electron affinity can be expressed through HOMO and LUMO energies as $I = -E_{\text{HOMO}}$, $A = -E_{\text{LUMO}}$. The hardness compounds to the gap between the HOMO and LUMO orbital energies. If the gap energy is higher than the Hardness is also larger. The global hardness $\eta = \frac{1}{2} (E_{\text{HOMO}} - E_{\text{LUMO}})$. The hardness is associated with the stability of chemical potential (μ) can be expressed in combination of electron affinity and ionization potential. The global electrophilicity index (ω) is also calculated (24) and listed in table- 4.

Table No: - 4 Comparison of HOMO-LUMO, Energy gap and related Molecular Properties of 2-amino,3-chloro 1,4-naphthoquinone

Molecular Properties	DFT
HOMO eV	-0.26066
LUMO eV	-0.15068
Energy gap	0.10998
Ionisation Potential (I)	0.15068
Electron Affinity(A)	0.26066
Global Hardness (η)	0.05499
Chemical Potential (μ)	0.20864
Global Electrophilicity (ω)	0.3958

**Fig. 2 : a) HOMO and b)LUMO of 2-amino,3-chloro 1,4-naphthoquinone**

Thermodynamic properties

On the basis of vibrational analysis at B3LYP / SDD and HF / SDD level, several thermodynamic parameters are calculated and are presented in Tabl-5. The zero point vibration energy (ZPVE) and the entropy, Svib.(T) are calculated to the extent of accuracy and the variations in ZPVE seem to be insignificant. The total energy and the change in total entropy of 2-amino,3-chloro 1,4-naphthoquinone at room temperature at different methods is only marginal (25-26).

Table 5 Theoretically computed Energies (a.u.), Zero point Energy (Kcal / mol) Rotational Constants (GHz),Entropy (cal mlo⁻¹K⁻¹) and Dipole moment D (Kcal. mlo⁻¹K⁻¹)

Parameter	DFT/B3LYP/SDD
Total Energy e.u.	-604.68 a.u.
Zero Point Energy	375424.8 (Joules/Mol)
Rotational constants(GHZ)	1.06888 0.52438 0.35234
Entropy Total	96.276
Translational	0.889
Rotational	0.889
vibrational	94.498
Dipole movement (D)	3.9351 Debye

4. Conclusions

This ligand has four donating atoms which are useful for biological various reactions. The calculated vibration frequencies are compared with experimental data and found most of them are in good agreement. The assignments were confirmed with the help of animation process which is available in Gaussian 09 computer code. The molecular geometry of 2-amino,3-chloro 1,4-naphthoquinone is best at the DFT/ SDD level. The HOMO- LUMO energy was calculated and other related molecular properties were also discussed. The

Mullikan atomic charges were calculated and the results were discussed. Thermodynamic parameters were calculated.

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