Regular Article

Theoretical calculations of infrared, NMR and electronic spectra of 2-nitroso-1, naphthol or 1-2 naphthoquinine-2 oxime and comparison with experimental data

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The geometry of the 2-nitroso-1,naphthol in solid state and 1-2 naphthoquinine-2, oxime in solution have studied by employing Hatree Fock ab initio calculations using 6-31 G* level. IR wave number of 2-nitroso -1, naphthol is calculated and compared with experimental date. Further, 1-2, naphthaquinine-2, oxime in solution, NMR chemical   shifts of ^{1}H and 13C are calculated by HF method and 6.31 G* level, experimental data was compared. Electronic spectra were also calculated and compared with experimental data. These results are discussed in detail in this work

Keywords: 2-nitroso-1-naphthol, 1-2 naphthoquinone-2-oxime, IR, NMR, Hartree Fock , Electronic spectra

2-nitroso-1, naphthol has great ability to form metal chelates and it is a sensitive and specific reagent for fluorimetric determinations of tyrosine residues in proteins & peptides (1). It also shows good cytotoxic action (2). This compound makes part of noxious substances in the different industries such as pharmaceutical preparations and pesticides (3). Proton transfer in a hydrogen bond is an elementary process presenting many systems of biological interest. Recent studies on proton dynamics in hydrogen bomb is appearing in literature (4-7). The nitroso-oxime tautomeric equilibrium was extensively studied by employing spectroscopic methods including UV (8-9) and NMR (10-40) a Krzan et.al. (15) reported a systematic ab initiao MO study of various structures based on 2 nitroso napthol to elucidate different factors. We present the results of Hartree – Fock MO calculations on 2- Nitro 1 naphthol for IR in solid state and the data is compared with experimental values. UV and NMR calculations were carried out in solutions i.e. for 1-2 napthoquinone-2 oxime and the data is verified with the experimental data.

Experimental

2-nitroso-1, naphthol is used as it is supplied by (Fluka, chemicals). IR spectra in KBr matrix was recorded on JASCO FTIR at room temperature. A far infra red spectrum in the region 700- 200 cm-1 was recorded on Nicolet 6700, Diamond ATR model. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Varian MR 400 MHz in DMSO_d$_{6}$ using TMS as standard. An

electronic spectrum was recorded in KBr matrix in solid state at room temperature on JASCO 530 model and also in different solvents.

Computational details.

The theoretical calculations of the 2-nitroso-1, naphthol and tautomer 1-2 naphthoquinine-2 oxime were carried out with SPARTAN 08 mechanics program. Geometry optimization was calculated using RHF / 6-31G* level basic set method. The harmonic vibrational frequencies and the IR intensities were calculated at the RHF / 6-31 G* level of theory. The wave number values computed by the HF method and 6-31 G* level contain known systematic errors due to negligence of electron correlation (11). We therefore have used the scaling factor as 0.90 for HF/6-31G* set. A restricted Hartree –Fork SCF calculation were performed using Pulley DIIS + Geometric direct minimization and frequency calculation were generated with standard thermodynamic parameters at 298.154 K and 1.00 atm.

Results & Discussions

Infrared spectrum

2- Nitroso -1-napthol exists in solid state so that its spectrum in KBr matrix is recorded at room temperature. Infrared wave numbers and the assignments are given in Table 1 along with the calculated and scaled wave numbers.

Table 1. Measured, calculated and scaled IR wave numbers of 2-nitroso-1, naphthol

Sr. No.	cm^{-1} Cal. HF	Int.	cm^{-1} Expt.	Int. %T	cm^{-1} Expt. Diamond ATR	Assignments
1	83.9817	0.26	--	--	--	--
2	150.9813	0.04	--	--	--	Wing-wagging o.p.
3	198.3627	3.82	--	--	--	Skeletal deformation
4	207.486	9.22	--	--	--	--
5	254.9124	1.47	--	--	248.03	--
6	289.9881	13.22	--	--	317.70	--
7	342.8577	3.43	--	--	345.58	Skeletal deformation
8	365.4045	0.92	--	--	--	--
9	440.0172	16.39	433.905	72.17	420.29	--
10	464.9184	4.62	458.975	81.89	--	Skeletal deformation
11	497.3859	2.39	485.974	63.20	485.33	v O-H
12	532.2141	2.60	532.257	90.39	--	Skeletal deformation
13	571.8249	1.88	578.54	80.34	--	Skeletal deformation
14	575.6265	125.08	578.54	80.34	--	Naphthalele skeleton
15	617.2974	56.09	609.396	92.68	614.30	--
16	645.9741	9.32	679.785	62.00	--	--
17	720.0243	2.40	--	--	--	O-H stretching
18	727.2198	32.50	--	--	--	--

19	739.4094	41.53	755.959	60.68	--	Skeletal deformation
20	793.3635	50.56	793.564	62.85	--	C-H bending
21	864.8874	50.39	849.49	74.93	--	v C-H
22	871.0713	5.65	878.41	90.64	--	Skeletal deformation
23	897.8013	20.52	888.059	84.96	--	C-H bending
24	901.6695	31.64		--	--	--
25	919.5705	16.65		--	--	--
26	990.2277	39.27	974.84	66.93	--	C-H bending o.p.
27	1042.007	3.45	1032.69	79.03	--	--
28	1074.533	0.26	--	--	--	--
29	1078.553	39.33	--	--	--	--
30	1094.485	157.89	--	--	--	--
31	1096.455	0.12	1093.44	70.34	--	Naphthalele skeleton
32	1154.917	151.75	1154.19	74.82	--	C-H bending i.p.
33	1168.975	88.74	1177.33	88.37	--	C-H bending
34	1198.823	3.91	--	--	--	C-H naphthalene skeleton
35	1203.534	27.64	--	--	--	--
36	1234.37	146.79	1233.25	87.27	--	C-H bending i.p.
37	1278.851	15.76	--	--	--	--
38	1297.528	2.65	1318.11	68.44	--	v CN
39	1379.545	29.70	1383.68	66.61	--	C=C stretching
40	1408.118	18.69	--	--	--	C=C stretching
41	1412.889	276.40	--	--	--	--
42	1453.491	2.81	--	--	--	C-C stretching
43	1470.042	2.03	1435.74	59.36	--	C-C stretching
44	1502.99	16.88	1551.45	78.15	--	N=O
45	1574.205	100.67	1594.84	73.80	--	C-C stretching
46	1603.149	22.26	1608.34	90.10	--	C-C stretching
47	1626.504	102.93	1668.12	54.76	--	--
48	3019.477	0.53	--	--	--	C-C stretching
49	3032.168	4.85	2858.95	61.28	--	Naphthalele skeleton
50	3035.967	12.88	2974.66	61.28	--	C-H stretching
51	3053.901	15.98	3077.83	63.52	--	v (C-H)
52	3069.081	3.85	3242.72	59.55	--	v (C-H)
53	3074.997	2.84	3739.3	89.62	--	v (O-H)
54	3471.179	154.10	3832.83	90.32	--	v (OH)

δ- In plane deformation,   ν- out of plane deformation, i.p. = in plane O.P. = out of plane

The three normal vibrations of hydroxyl group are ν OH, δ OH and γ OH and the out of plane deformation vibrations are group vibrations (16). The Hartree –Fock calculations predict ν OH, mode vibration at about 3471 cm^{-1} and the observed band at 3832 cm[-1.] Generally phenols absorb at 1350±50 cm [-1] and it is assigned for δ OH vibration (17) and is observed 1383.6 cm^{-1} which is similar to HF predicted band at 1375.5 cm[-1.] The vibration band for OH out of plane deformation is predicted as 720 cm [-1] by HF calculation which observed at 679.7 cm [-1] and it is expected in the range of 685 ±115 cm [-1] for phenols (16) The nitrogen from N=O is directly attached to the ring carbon the stretching vibration of the C-N bond is expected in the range of 1260-1330 cm^{-1} (17, 18) in HF calculation these band is predicted at 1297.5 cm[-1.] And in present case, it is observed at 1318.1 cm^{-1}. It is reported that the band at 1268 cm^{-1} is assigned to C-N stretching vibration in the Raman spectrum of paraphelylene diamine (19). Aromatic nitroso compounds absorb IR radiations in the range of 1511- 1495 cm^{-1} for the vibration of N=O, the band at 1502.9 cm^{-1}is predicted in the Hartree-Fock calculation and this band is found presently at 1541.4 cm^{-1}.

C-H stretching frequencies
The frequencies in naphthalene are reported (20) at 3027, 3055 7 3060 cm^{-1} for C-H stretching vibration and are assigned to a$_1$ type symmetry. In the present work, these peaks are found at 2858, 2974 & 3077 cm^{-1}. The remaining frequency at 3242 cm^{-1} can be assigned to b$_2$ fundamental. IR frequencies of sodium salt of 1-nitroso-2- naphthol-6- sulphonic acid for C-H bending are reported by Siren et.al. (21) as naphthalene skeleton at 3060, 2920, 2640, 1297, 1110 & 590 cm [-1].The HF calculation have predicted these values at 3077, 2858, 1297, 1096 and 575 cm^{-1}. The remaining frequencies are assigned according to work reported by Singh et. al. (22). The FAR IR spectrum of 2-nitroso-1, naphthol is shown in Fig-1.
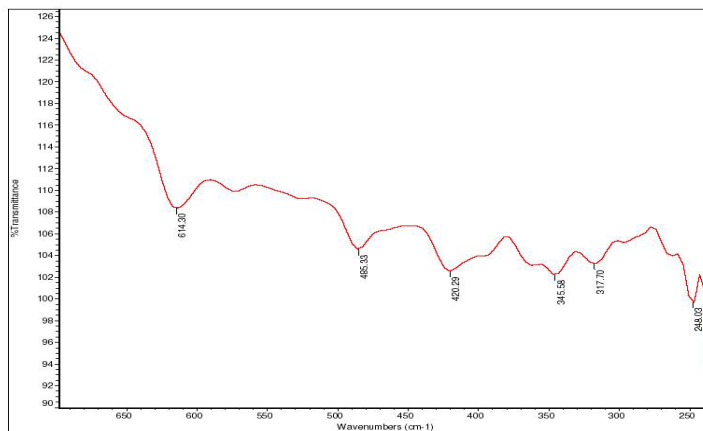

Fig-1 Far IR spectrum of 2-nitroso-1, naphthol

Nuclear Magnetic Resonance
Proton NMR and ^{13}C NMR shifts have been calculated by HF method with help of Fig-2 and using SPARTAN08 quantum mechanical program at 6-31G* level. The molecular geometry is optimized by restricted Hartree-Fock method with 6-31G* level & SCF model. The chemical shifts of protons of 1-2 naphthoquinone -2-oxime which is a tautomer of 1-nitroso-2-naphthol. It exits in solution so that the chemical shifts are calculated in CD$_2$Cl$_2$ and in DMSO solvents. The δ values in ppm are tabulated in Table-2. The chemical shift of oxime proton i.e. H$_7$ is predicted by theoretical calculation is at 8.17 and 8.84 ppm in CD$_2$Cl$_2$ and in DMSO solvents respectively. The observed chemical shift is 13.6 ppm in DMSO_d$_6$. This δ value is reported as 11.0 ppm in

solution by Andrew E. Shchavlev et. al. (23,24) and 13.7 ppm is observed by T. Shono et.al. (11) which is comparable with the present work.
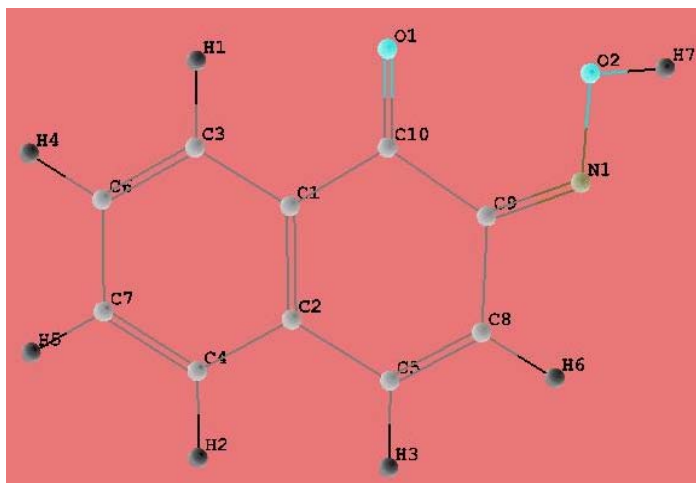

Fig -2 Optimised structure of 1-2 naphthoquinone -2-oxime

Table 2: Chemical shifts of Proton NMR of 1-2 naphthoquinone-2 oxime in ppm

Sr.No.	Atom	δ Cal. CD_2Cl_2	δ Cal. DMSO	δ Expt. $DMSO\_d_6$
1	H1	9.02	8.98	8.34
2	H2	7.22	7.53	7.54
3	H3	6.84	7.66	7.03
4	H4	7.52	7.72	7.53
5	H5	7.65	7.98	7.61
6	H6	6.58	6.77	6.66
7	H7	8.17	8.84	8.19

Table-3 shows chemical shifts of ^{13}C NMR Spectrum of 1-2 naphthoquinone-2 oxime $DMSO\_d_6$ in ppm and calculated data in CD_2Cl_2 and in DMSO.

Table 3: Chemical shifts of ^{13}C NMR Spectrum of 1-2 naphthoquinone-2 oxime in ppm

Reno.	ATOM	δ Cal. CD_2Cl_2	δ Cal. DMSO	δ Expt. $DMSO\_d_6$	Ref. No. 23
1	C1	121.01	120.36	127.88	
2	C2	124.10	124.58	126.98	
3	C3	122.91	122.84	122.2	
4	C4	116.54	115.44	115.94	
5	C5	119.35	119.34	126.28	
6	C6	117.81	116.85	125.57	
7	C7	124.94	124.24	132.91	
8	C8	118.29	116.48	122.22	
9	C9	140.16	143.05	145.29	155.5
10	C10	170.02	172.84	184.36	183.9

DCM = Dichloromethane   DMF = Dimethyl formamide

The B3LYP optimized geometrical parameters (bond length in A^0 and Bond Angle in degree) of 1-2 naphthoquinone-2-oxime are presented in Table-4.

Table 4 Bond length and bond angles of 1-2 naphthoquinone-2-oxime

Bond length	A^0	Bond Angle	Deg. (^{o})
C_9N_1	1.306	$H_7O_2N_1$	103.12
N_1O_2	1.393	$O_2N_1C_9$	113.05
O_2H_7	0.974	$N_1C_9C_{10}$	126.38
C_9C_8	1.485	$C_9C_{10}O_1$	122.95
C_8H_6	1.085	$O_1C_{10}C_1$	119.22
C_8C_5	1.336	$H_1C_3C_1$	120.32
C_5H_3	1.086	$C_{10}C_1C_3$	119.63
C_5C_2	1.460	$H_1C_3C_6$	119.62
C_2C_1	1.399	$H_4C_6C_7$	120.19
C_1C_{10}	1.482	$C_7C_4C_2$	120.52
$C_{10}O_1$	1.223	$C_4C_2C_1$	119.01
$C_{10}C_9$	1.535	$C_2C_1C_3$	120.42
C_1C_3	1.402	--	--
C_3C_6	1.394	--	--
C_6C_7	1.393	--	--
C_7C_4	1.397	--	--
C_4C_2	1.402	--	--

Electronic spectra

The ultra violet spectra is calculated by restricted Hartree – Fock method at optimized geometry and different electronic transitions are predicted in vacuum for 2-nitroso-1-naphthol as well as for 1-2 napthoquinone-2-oxime in DMSO solvent which is tabulated in Table-5 along with experimental uv absorption data in the range of 200-800 nm.

Table 5: Electronic spectra of 2-nitroso-1-naphtol in solid, in solution and calculated data

λ max nm calculated	λ max nm in KBr	λ max calculated tautomer oxime form	λ max nm in Methanol	λ max nm in Chloroform	Assignment
174.6	--	174.2	--	--	--
191.0	--	183.4	--	--	--
224.7	231.0	213.0 221.0	--	--	π to π*
243.7	--	253.0	260.0	260.0	π to π*
--	304.0	--	346.0	--	π to π*
--	402.0	--	--	--	n to π*

QET = Quinonoide electronic transition

The calculated maximum absorption transition peaks are at 224.7 and 243.7 nm while the experimental observed peaks are at 231.0 & 304 nm which are assigned to π to π* and the peak at 402.0 nm is assigned to n to π*. The calculated UV transitions for 1-2 naphthoquinone-

2-oxime are at 174.1, 183.4, 213.0, 221.0, 253.0 and 328.2 nm. The calculated peaks at 213 & 221 nm shows splitting as compared to 217 nm in methanol and the predicated transition at 153 nm is in good agreement with the observed transition at 260 nm in methanol & chloroform. Similar work is reported for 1-2 naphthq2ouinone-2 oxime in water – ethanol for maximum absorption at 261 nm in acidic medium at pH 1 to 5 as well as the maximum at 278 nm in neutral and basic media. These transitions are due to π* transition within the orthoquinone oxime system (8). The transition at 345 nm in methanol is characteristics of o-benzoquinone while this peak is observed in chloroform. The maximum absorption at 415 nm in chloroform is associated with the intramolecular ligands charge resonance.

Conclusions
In this work, we have performed the theoretical and experimental infra red vibrational analysis of 2-nitroso-1-naphthol, and its oxime tautomer, NMR data is used to describe structural aspects. The theoretical study gave a description of the geometry and vibrational wave numbers of the title compound. The calculated data is in good agreement with the experimental values for the investigation of 2-nitroso-1-napthol molecule. Electronic spectra is calculated and compared with experimental values which are in good agreement. This data is useful to explain reactivity of the molecule.

Acknowledgements

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