Regular Article

Synthesis, spectral and Theoretical investigation on 1-2 naphthoquinone dioxime

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The structure of 1-2 naphthoquinone dioxime is examined by use of the HF (6 -31 G* level), density functional theory DFT (6 -31 G* level) & hybrid functional B3LYP. Using the optimized structure of the titled compound IR, NMR, and ultraviolet data is calculated and compared with experimental data. It shows good relation between theoretically calculated IR wave numbers & observed values for Mid – Far IR data. The chemical shifts are in good comparison for ^{1}H & ^{13}C spectra and electronics spectra also. The results are discussed in this paper.

Keywords: 1-2 naphthoquinone dioxime, FAR-IR, MID – IR, NMR, UV spectral, HF & DFT

The chelate formation ability of the –C (=NOH)-C (=NOH)-group is greatly influenced by the special arrangement of the two oxime groups and this property have been the subject of many investigations during the last few decades. The co-ordination chemistry of metal chelates of vic-dioximes has been studied well and is the subject of several reviews published in literature (1, 4).

It has been found that biological systems have great influence by dioximes such as vitamin B12 (5-7). Many oxime compounds and their metal chelates have shown notable bio activity as chelating therapeutres, as drug, as inhibiters of enzymes as well as intermediates in the bio synthesis of nitrogen oxides and other important biomaterials (8-9). The antimicrobial activities tend to differ according to ring size, a better antimicrobial activity being obscured in the case of chelates having six member rings (10). The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms make vic-dioximes amphoteric ligands that form corrin type, square planner, square pyramidal and octahedral chelates with transition and rare earth metal ions (11). Antimicrobial activity of transition metal complexes of 3-hydroxyimino-5-methyl-2-hexanone and 5-methyl-2, 3-hexanedione dioxime have been reported by Donde et.al. (12). Among the 3 isomers, namely anti, amphi and syn, the first is more liable to form N, N coordinated planner chelates stabilized by hydrogen bonding (13). in the research area of bioinorganic chemistry, transition metal chelates can probe nucleic acids with oxime and dioxime bases is a prominent one (14-16).

Copper complexes are well established as chemical nucleases and known to cleave DNA by hydrolytic mechanism (17) and also by oxidative mechanism (18-19). Antimicrobial activity of metal chelates of 2-hydroxy 1-4, naphtholenedione-1-oxime is reported by S.B.

Jagtap et.al. (20). The theoretical calculations 0f 5 - hydroxyl 1-4, naphthoquinone (Juglone) have been reported by A.B. Pawar et.al. (21). Dioximes, generally forms chelates of anti isomers but it has been stated that aromatic rings destroy such action and no scarlet coloured chelates is formed by the dioximes of 1,2 naphthoquinone (22) for which stable amphi configuration could be expected. To have structural arrangement of oxime groups, theoretical calculations are preferred by optimizing the geometry of the molecule. Also theoretical calculations of the IR wave numbers, NMR proton and ^{13}C chemical shifts and electronic spectra are carried out by employing Hartree-Fock mechanical program at 6-31 G* level. The calculated data and experimental results are compared in this work.

Materials and Methods

Synthesis of 1-2napthoquinone dioxime was carried as per the reported method (5) which was recrystalized using methanol. All the chemicals were analytical grade. IR spectra were recorded on JASCO FTIR 4100 spectrophotometer in Ker matrix in the range 4000-400 cm^{-1} and far infrared spectra recorded on Nicolet 6700 with diamond ATR in the range of 550 to 150 cm^{-1}. UV spectra were recorded on JASCO 530 model in different solvent as well as in solid state in KBr matrix. Proton NMR and ^{13}C was recorded on Varian MR-400 MHz in CDCl$_3$

Computational details

Theoretical calculation were carried out with SPARTAN 08 program using the DFT (B3LYP/ 6-31G* and RHF (6-31 G*) levels of theory to predict the molecular structure and wave numbers in IR, UV region and NMR chemical shifts by employing geometry optimization. A restricted Hartree Fock SCF calculation was performed using Pilay DIIS+ Geometrize Direct Minimization. The wave number values computed theoretically contain known systematic error due to the negligence of electron correlation (6). We therefore have used the scaling factor as 0.90 for HF/6-31G* set for calculation of IR wave numbers.

Results and Discussion
Infra red region

The infrared spectra of 1-2-naphthoquinone dioxime is calculated by HF method and employing 6-31G* level and IR spectrum recorded in KBr matrix as well as FAR IR in the range of 700-200cm^{-1}, the data for wave numbers and their assignments are given in Table 1.

The title compound has the oxime groups ie. each has –OH group which generally provides three normal vibrations as vOH, δOH and γOH. Naphthoquinone also show CH stretching vibrations but also out of plane deformations are good group frequencies (23). The HF calculations predicted mainly two δ absorption maximum band at 38636 and 3866.7cm^{-1} for vOH and the observed band is at 3852.1 and 3748.9 cm^{-1} which is in good agreement. The another important OH peak is predicted at 1386.2 cm^{-1} by HF calculation while this peak is observed at 1383.7 cm^{-1} which is assigned for ∂OH. This is supported by the absorption peak for δOH in phenols is in the range of 1350±50 cm^{-1} (24). The vibration band for OH out of plane deformation is predicted at 743.4 cm^{-1} which is observed in the present work at 755.9 cm^{-1}, this band is supported by the literature value in the range of 685 ±115 cm^{-1} for phenols (24). The vic dioximes in the solid state show the O… H-O bonding (25-29) at about 1700±50 cm^{-1} and similar bond is observed at 1669.0 cm^{-1}. The characteristic stretching vibration belonging to C=N were presented in the range of 1610-1655 cm-1 (26, 27). The HF calculations have predicted C=N at 1688.5 cm^{-1} which is comparable to the experimental value 1669.0cm^{-1}. Both the results are in good agreement. The other stretching vibration of N-O of the oxime group is

reported in the range of 970-990 cm^{-1} and the observed value is at 973.8 cm^{-1} which is comparable to calculated absorption band at 950.6cm^{-1}. The CH stretching frequencies of naphthalene are reported at 3027, 3055 and 3660 cm^{-1} and are assigned to type symmetry (30). For this vice dioxime of naphthalene, we observed absorption maxima at 2864, 2972, 3246 cm^{-1} for CH stretching. On the other hand the calculated absorption peaks are predicted at 3351, 3361, 3365 and 3382 cm^{-1} and these values are higher than reported one. The other important absorption peaks for CH bonding are reported by Siren et.al. (31) as naphthalene skeleton at 1290, 1110 and 590 cm^{-1}. All other bands are assigned according to reported data (32).

Table: 1 IR wave numbers of 1-2 naphthoquinone dioxime experimental and calculated

Sr. No.	Species	cm^{-1} Cal.HF	Int.	cm^{-1} Expt.	Intensity	Far IR cm^{-1} Expt.	Assignments
1	A″	76.554	0.03	--	--	--	--
2	A″	112.356	0.23	--	--	--	--
3	A″	160.016	1.11	--	--	--	Wing wagging o.p.?
4	A′	172.946	0.73	--	--	--	--
5	A″	282.752	0.00	--	--	244.4	--
6	A″	308.245	28.13	--	--	--	--
7	A′	310.818	0.86	--	--	--	--
8	A′	337.484	0.04	--	--	--	--
9	A″	377.074	125.87	--	--	--	--
10	A″	394.131	1.00	401.121	66.95	391.6	OH torsion
11	A′	426.293	9.73	424.263	66.30	415.9	--
12	A′	467.278	1.70	--	--	--	--
13	A″	468.838	149.31	471.51	82.98	--	--
14	A″	491.891	30.61	491.759	80.58	483.9	--
15	A′	584.578	5.46	578.54	88.76	572.0	CH bending
16	A′	602.558	23.46	--	--	--	--
17	A″	622.561	2.02	623.859	86.48	617.9	--
18	A″	650.683	41.12	653.75	82.98	652.7	--
19	A′	662.766	0.32	679.785	73.52	677.1	--
20	A′	743.444	7.12	755.959	61.72	--	γ OH
21	A″	829.032	10.29	818.634	75.35	--	--
22	A′	831.942	0.32	849.49	77.20	--	--
23	A″	884.665	50.37	890.952	85.92	--	--
24	A′	921.017	34.79	934.342	70.98	--	CH bending o.p.
25	A″	950.697	57.17	973.876	69.68	--	NO oxime
26	A′	1009.216	18.36	--	--	--	Skeletal deformation i.p.
27	A′	1037.303	68.14	1031.73	86.03	--	CH bending o.p.
28	A″	1059.907	2.52	1068.37	79.43	--	CH bending o.p.
29	A″	1080.198	95.85	1093.44	77.65	--	CH bending n.s.
30	A′	1137.225	44.01	1137.8	81.65	--	--
31	A″	1148.412	5.62	--	--	--	CH bending i.p.
32	A′	1156.372	49.27	1156.12	83.18	--	--
33	A″	1190.452	0.01	--	--	--	--

34	A″	1202.921	0.20	--	--	--	--
35	A′	1219.652	8.12	--	--	--	--
36	A′	1246.605	1.92	--	--	--	--
37	A′	1246.605	6.86	--	--	--	--
38	A′	1309.496	11.85	--	--	--	--
39	A′	1328.057	3.09	1318.11	74.64	--	CH bending n.s.
40	A′	1355.201	12.70	1338.36	75.53	--	--
41	A′	1388.125	0.93	1383.68	72.41	--	δ-OH
42	A′	1438.308	17.85	1436.71	70.32	--	--
43	A′	1488.441	240.71	--	--	--	--
44	A′	1501.524	13.04	1540.85	82.65	--	CC stretching
45	A′	1572.614	5.82	1594.84	81.97	--	CC stretching
46	A′	1620.975	8.65	1608.34	89.90	--	--
47	A′	1658.508	21.79	1669.09	72.61	--	O---H-O
48	A′	1739.570	0.08	--	--	--	--
49	A′	1770.311	5.08	--	--	--	--
50	A′	1844.468	6.31	--	--	--	--
51	A′	1865.695	4.35	--	--	--	--
52	A′	1877.923	1.36	--	--	--	--
53	A′	3351.110	1.35	2342.12	77.03	--	--
54	A′	3361.127	2.79	2358.52	71.32	--	--
55	A′	3365.297	20.67	2864.74	76.32	--	νC-H stretching
56	A′	3382.745	23.27	2972.12	77.03	--	νC-H stretching
57	A′	3409.137	4.46	3246.57	78.35	--	νC-H stretching
58	A′	3432.372	2.26	3491.49	86.17	--	--
59	A′	3863.668	112.58	3748.94	88.78	--	νO-H stretching
60	A′	3866.776	93.62	3852.11	90.69	--	νO-H stretching

δ- in plane deformation, ν – stretching, γ= out of plane deformation
i.p. inplane   o.p. out of plane   n.s. naphthalene skeleton

FAR IR Spectra

The FAR IR spectra of the titled compound are presented in Fig. 1. The OH torsion frequency of oxime is predicated at 294.1 cm^{-1} and the recorded frequency is 391.6 cm^{-1}. Generally OH torsion frequency of oxime group is observed in the range of 380±15 cm^{-1} (33).
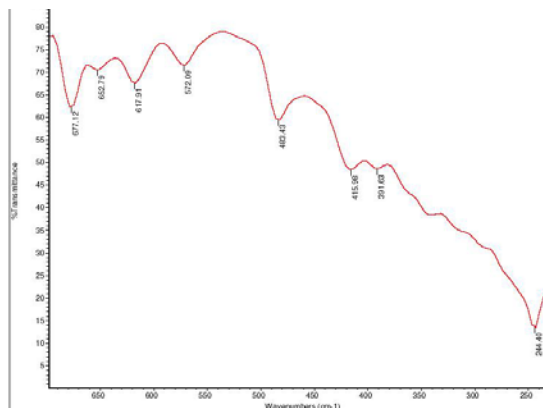

Fig. 1 FAR IR spectrum of 1-2 naphthoquinone dioxime

NMR Spectroscopy:
Proton NMR

The chemical shifts of protons of the vic dioxime of naphthalene have been calculated by HF method using Fig-2 and the δ values are tabulated in Table 2 and the experimental chemical shifts are observed in DMSO-d6.
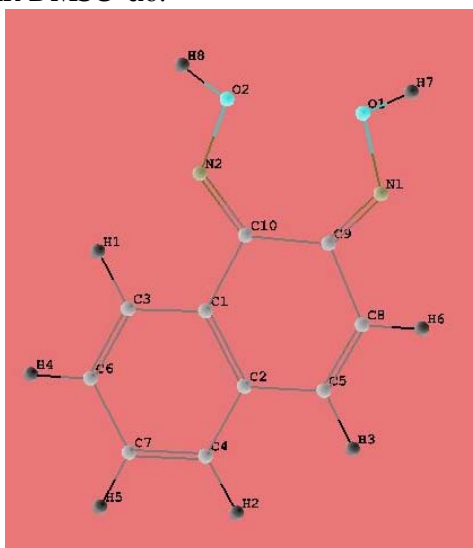

Fig: 2 Sketch of dioxime

Table: 2 Chemical shifts of ^{1}H NMR of 1-2 naphthoquinone dioxime

Sr.No.	atom	δ Cal. In DMSO	δ Expt. in DMSO
1	H1	8.39	8.21
2	H2	7.27	7.51
3	H3	7.20	7.14
4	H4	7.50	7.71
5	H5	7.60	7.76
6	H6	6.30	6.63
7	H7	8.53	13.62
8	H8	8.47	13.28

DMSO=Dimethylsulphoxide

The oxime proton of C10 and C9 i.e. H_7, H_8 have calculated chemical shift at 8.47 and 8.53 ppm but the observed values are at down field indicates at 13.28 and 13.62ppm. The chemical shifts of H_1 to H_6 which are attached to naphthalene skeleton are observed in good agreement to the calculated data and in the range of ± 0.5 ppm.

13C NMR

The chemical shift of 13C NMR of vic dioxime i.e. 1-2 naphthoquinone dioxime are given in Table 3 calculated and observed δ ppm values. The chemical shift of C_9 and G_{10} are calculated as 137.3 and 135.5 ppm but the observed values of δ ppm are downfield at 145.2 and 136.37 ppm. Here C_9 and G_{10} is a cause of C=N bonding of oxime group which is a most indicative of

the quinonide structure. The chemical shifts of C_1 to C_8 are observed higher i.e. lower field by a range of ± 10-15 ppm as compared to calculated data. The DEPT data of ^{13}C is also given in Table- 2 for the carbons C1 to C8.

Table: 3 Chemical shifts of ^{13}C NMR of 1-2 naphthoquinone dioxime

Sr. No.	ATOM	δ cal. in DMSO	δ Expt. in DMSO	DEPT
1	C1	121.05	134.66	134.67
2	C2	121.01	129.46	129.46
3	C3	119.42	130.24	130.24
4	C4	117.16	126.30	126.30
5	C5	118.90	129.11	129.46
6	C6	117.84	128.91	128.42
7	C7	120.45	132.93	132.94
8	C8	119.33	130.23	130.56
9	C9	137.33	145.29	--
10	C10	135.54	136.37	--

DMSO dimethyl sulphpoxide

Table: 4 B3LYP optimized geometrical parameters

Bond length	A°	Bond angle	Deg. (°)
C9N1	1.311	C9N1O1	117.37
N1O1	1.377	N1O1H7	103.13
O1H7	0.973	N1C9C10	133.37
C9C10	1.547	C9C10N2	130.32
C10N2	1.306	C10N2O2	117.68
N2O2	1.376	N2O2H8	103.23
O2H8	0.973	N2C10C1	113.29
C10C1	1.515	N1C9C8	110.51
C1C2	1.397	C9C8C5	123.97
C2C5	1.452	C8C5C2	121.94
C5C8	1.332	C2C1C10	121.11
C8C9	1.495	C3C2C1	-30.65
C1C3	1.408	C1C3C6	120.95
C3C6	1.396	--	--
C6C7	1.390	--	--
C7C4	1.395	--	--
C4C2	1.405	--	--
C8H6	1.086	--	--
C5H3	1.086	--	--
C4H2	1.088	--	--
C7H5	1.087	--	--
C6H4	1.087	--	--
C3H1	1.088	--	--

Optimized data

The title compound was minimized and the B3LYP optimized geometrical parameters were calculated and the values for bond length in angstrom and bond angle in degrees are given in Table 4. The most important distances of C_9N_1 and $G_{10}N_2$ are calculated as 1.311 and 1.306A^0 which is highly comparable to the data presented by M. Nasakkala et.al (34) for the crystallographic data at C=N   (1.304 and 1.306A^0). Similarly N-O distances are calculated as 1.377 and 1.376 A^0 while reported values are 1.394A^0 and 1.379A^0 and which are closely equal. These values compare well with the corresponding bond lengths found in several other oximes: 1.30 ± 0.02 and 1.38 ± O.2 A^0. The CNO angle in typical oximes is relatively constant around 112-113^0 (1, 35). The calculation predicted $C_9N_1O_1$ angle at 117.37^0 and the $C_{10}N_2O_2$ at 117.48^0 while x-ray diffraction data of this title compound showed 117.0^0 and the $C_{10}N_2O_2$ is in the range (34). The bond lengths & bond angles are calculated and presented in Table 4.

Electronic Spectra

The ultra violet and visible spectrum is calculated by restricted HF method and the transitions are predicted in DMSO for 1, 2 naphthoquinone dioxime. The absorption maxima of the titled compound are determined in methanol, chloroform and in KBr matrix. The calculated and observed values of absorption are given in Table 5 along with possible assignments.

Table 5: Electronic spectra of 1-2 naphthoquinone dioxime in methanol and calculated data

λ max nm calculated in DMSO	λ max nm in KBr	λ max nm methanol	λ max nm Chloroform	Assignment
153.3	--	--	--	π to π*
163.7	--	--	240.0	π to π*
183.1	--	--	--	π to π*
212.6	--	224.0	--	π to π* BET
249.8	253.0	266.5	240.0 269.0	π to π* BET
--	307.0	358.0	360.0	π to π* OXIME
--	406.0	--	--	n to π*

BET = Benzeniode electronic transition

The calculated X max in nm are found to be at 153.3, 167.7, 183.1, 212.6 and 249.8nm. The determined data in KBr matrix is 253, 307 and 406 nm out of these values only 253nm is compared with calculated max at 249.8nm which is assigned as π to π* also known as benzeniode electronic transition. Also at 307nm is π to π* and the other at 406nm is due to n to π*. The maximum absorption at 406nm in KBr matrix is associated with the intra molecular ligands charge resonance. In methanol, it shows the absorption bands at 224 and 266.5nm which are assigned to π to π*   transition and it is designated as benzeniode electronic transition. Similarly in chloroform these bands are observed at 290 and 269nm. In this case, it shows the effect of solvent as the absorption maxima. The absorption maxima observed at 358 and 360nm in methanol and chloroform are due to π to π*   which is due to C=N of the oxime group.   The maximum absorption is moving to longer wavelength as compared to the

maximum absorption in chloroform of the 1, 2 naphthoquinone 2 oxime (36). The vic dioxime required less energy as the amount of delocalization increases.

Conclusions

The IR wave numbers calculated are well comparable to experimentally observed results. A far infrared spectrum is presented and it gives valuable information. Proton NMR and ^{13}C NMR chemical shifts are in good agreement with the calculated data. Optimized geometry parameters are compared with x-ray diffraction data for bond length and band angles and it has given good information of the structure of this vic dioxime. Electronic spectra shows a maximum absorption band for π to π* at 406nm only in solid state. In solvents, we observed benzeniode, oxime transition of the titled compound.

Acknowledgement

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