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Synthesis And Characterization Studies Of Some 1, 4-Naphthoqunione Substituted C_1-NOH, C_2-NH_2 And (N-Acetyl) Acetamido

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Abstract: *Amino quinones are used as medicines, herbicides and redox switching properties. Amino quinones are formed in the reaction of different amines with 1, 4- naphthoquinone . Synthesis of 2-amino-1, 4-napthoquinone (L1), 2-(N –acetyl) –acetamido-1, 4- naphthoquninone. (L2). 2-amino-1, 4-napthoquninoe-1 oxime (L3). and 2-(N-acetyl)-acetamido-1, 4 naphthoquinone -1, oxime (L4) were carried out. X-ray diffraction studies show that all the ligands are crystalline in nature and belong to triclinic group. Crystalline parameters and h , k, l values are calculated by using McMallie computer code. The crystalline size is determined by Scherrer formula and found to be L1 – 86.29nm, L2-57.51nm, L3 – 46.54nm and L4-34.81nm .The results are discussed in this paper.*

Keywords : *2-Amino-1, 4-naphthoquinone, XRD, IR *To whom correspondence should be made*

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I. Introduction

2- Amino-1, 4-naphthoquinone is useful as electron mediators for enzyme immobilized anodes for field cells (1). It is used by intermediates for microbicides , drugs , agrochems etc (2). Introduction of amino at C_2 position can exert influence on its redox properties inducting oxidative stress in cells and alkylation of DNA. These compounds found in important bioactive compound such as antimalerial agent (3 - 4). Because of interesting biological activities of amino napthoquinone review have been published by Asharf A. Aly et. al. (5). The review includes synthetic methodologies for these classes in addition to their hetero cyclization process. They have described different schemes for the synthesis of about 300 derivatives of 2-Amino-1; 4-naphoquinone and related quinines were synthesized and investigated for carcinostatic activity. Relationship between structure and inhibition of tumor growth were shown and an attention is drawn to the fact that the carcinostatic quinone which are effective against the Ehrich carcinoma and the crocersarcoma 180 of the mouse do not belongs to the like trenion and similar ethyl amino quinones to the group of alkylating agents (6). Radical anions are the intermediates of several bio-organic and chemical processes. These species can be formed by transfer of a single electron to a neutral molecule or by a hemolytic cleavage of a bond from an anion. . Radical anions are present in several chemical processes and understanding the reactivity of these species may be described by their thermodynamic properties. The occurrence of unexpected anions was described as being a reaction between the solvent system and the radical ion. This is an important to understand the formation and reactivity of radical ions to establish the reaction between them (7). FTIR data of 5-amino 1-4 naphthoquinone is reported by Hong Li et. al. in KBr matrix as well as proton NMR data is given (8). Electronic spectra of 2-amino 1-4 naphthoquinone is given by Kenneth H. Dedly et . al (9). They have reported electronic transition bands at about 282, 334 and 462 nm NMR data of one proton is reported by ring hydrogen. We have synthesized 2-amino 1-4 naphthoquinone (L1) , 2 (N-acetyl)-acetamido-1,4-naphthoquinone (L2), 2-amino 1-4 naphthoquinone -1-oxime (L3) and 2 (N-actyl) -1,4-naphthoquinone -1-oxime (L4) and their characterization is carried out by X-ray diffraction, infrared spectroscopy as well as UV visible spectroscopy. The results are discussed in this paper.

II. Materials and Methods

Synthesis of 2-amino -1, 4- naphthoquinone was carried out as per the procedure given by Chrysostomos Pachatouridis et .al. (10) . 2 (N-acetyl)-acetamido -1,4-napthoquinone was prepared by the processes described by Ngoc-Chau.Tran et. al. (11). Synthesis 2-amino-1, 4- naphthoquinone -1 oxime and 2(N-acetyl)-acetamido-1, 4-naphthoquinone -1, oxime was carried out as per reported method (12).

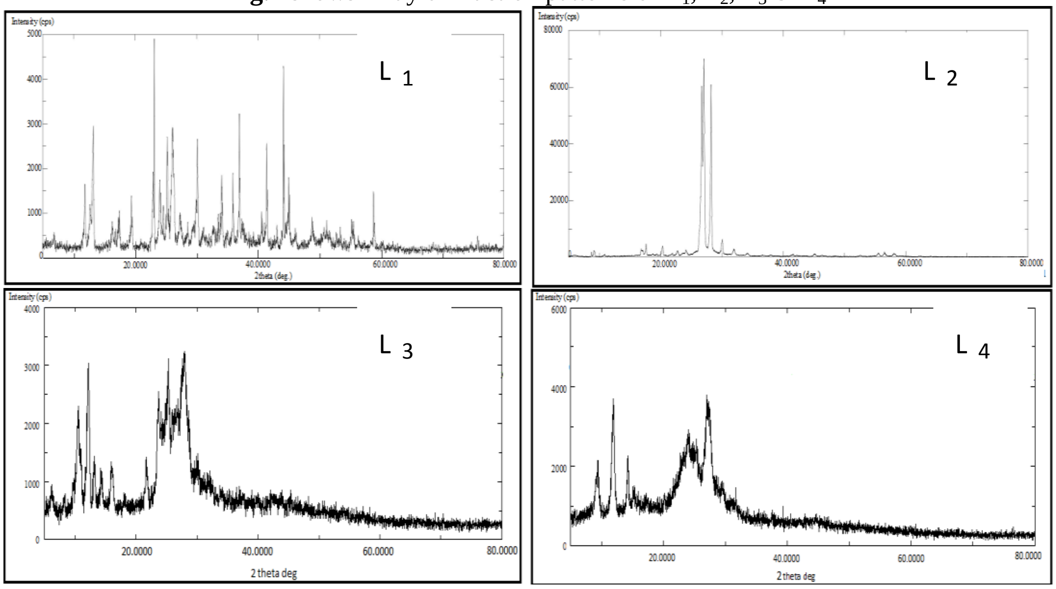
2.1 Instrumental analysis

The C, H, N analysis was carried out on ThermoFinnigan. X-ray diffraction patterns were obtained on Rigaku model 4 miniflex using Cu-K-α radiation (1.5404 A^0) at room temperature. IR spectra were recorded on a JASCO FTIR in the range 4000-400 cm^{-1}. UV –Vis spectra were recorded on JASCO 530 model in DMSO.

3.0 Results and Discussion:

3.1 X-ray diffraction;

Fig.1 shows x-ray diffraction patterns of L_1, L_2, L_3 & L_4



The crystalline structure of 2 - amino-1, 4-naphthoquinone has been determined by X-ray diffraction method. The crystal is monoclinic ($P2_{1/C}$). Three-dimensional integrated intensity data were collected on retigrams and operated by computers. The hydrogen bonds were deduced both form the location of the hydrogen atoms and from the distance between possible acceptors and donors (13). X-ray data such as d value and intensity ratios of $L_{1,}L_{2,}L_3$ and L_4 is given in table -1

Table-1- d value and Intensity ratios of $L_{1,}L_{2,}L_3$ and L_4

L_1		L_2		L_3		L_4	
d-value	I/Io	d-value	I/Io	d-value	I/Io	d-value	I/Io
7.4683	26	10.1091	3	8.3864	59	9.6465	33
7.0642	10	9.6675	4	8.0513	34	9.3808	40
6.9754	18	9.5631	3	7.2487	87	7.4308	96
6.7119	45	8.1102	2	6.7119	31	6.2059	49
5.4071	8	5.2729	4	6.2059	23	5.8471	25
5.2791	6	5.1751	4	5.5485	27	5.5554	21
4.6046	7	5.0293	7	5.4803	26	4.3967	23
4.5717	24	4.7312	2	4.0958	31	4.2752	20
4.5392	14	4.5952	2	3.7542	71	4.0883	32
3.8736	33	4.5717	2	3.6867	57	4.0225	33
3.8438	100	4.3625	6	3.5843	68	3.9004	52
3.7018	29	4.0920	2	3.5146	87	3.8081	59
3.6807	15	4.0515	2	3.4268	65	3.7448	62
3.6480	11	3.9208	3	3.3732	64	3.7048	75
3.6187	18	3.9004	3	3.3189	67	3.5092	65
3.5283	50	3.7762	2	3.2524	78	3.3508	60
3.4956	15	3.7386	2	3.2292	88	3.2996	100
3.4165	47	3.6837	4	3.1862	100	3.2408	90
3.4036	49	3.6450	2	3.1597	78	3.1271	33
3.3833	31	3.5092	2	3.1143	59	3.0974	31
3.2687	15	3.4902	3	3.0436	29	3.0335	33
3.1228	11	3.4529	3	2.9665	30	3.0035	32
2.9626	52	3.4216	3	2.9455	28	2.8238	22
2.8915	8	3.3858	14	2.8608	22		
2.8697	8	3.3336	94	2.8134	25		
2.8151	6	3.3044	79				

2.7477	9	3.2901	100				
2.7314	9	3.1575	92				
2.7201	10	3.0953	4				
2.6452	17	2.9820	7				

The crystal structure of Zinc Lawsonate and Lead Lawsonate belongs to triclinic group and the data is given by A. B. Pawar et. al. (13). The crystal structure of Zinc Juglonate and Lead Juglonate belongs to triclinic group of the data is given by A. B. Pawar et. al. (14). The crystal structure of lawsone monoxime is monoclinic group (15). It is observed that all the ligands are crystalline in nature. The data was processed by using McMaille computer program for determination of cell parameters. L_1 crystallizes in the triclinic group and it has crystalo graphic parameters such as .a = 14.5871A^{0,} b = 13.0005A^0, and c = 7.6897A^0, α = 93.294A^O, β = 75.683^O, and γ =101.877^O. Its volume is 1382.712 (A^0)^3 and its minimum density is Dmin= 3.363302g/cm^3. Calculated and measured h, k, l data is given in table number 2

Table - 2 h, k, l values of L_1

h	k	l	TH(OBS)	TH(ZERO)	TH(CALC)	DIFF	d value
1	0	1	11.840	11.840	11.845	-0.004	7.4683
1	1	1	12.680	12.680	12.664	0.016	6.9754
0	0	2	13.180	13.180	13.201	-0.021	6.7119
0	2	2	19.540	19.540	19.541	-0.001	4.5392
1	-1	-2	22.940	22.940	22.924	0.017	3.8736
2	1	1	23.120	23.120	23.108	0.012	3.8438
0	2	-3	24.020	24.020	24.023	-0.003	3.7018
1	3	2	24.160	24.160	24.143	0.017	3.6807
0	3	-2	24.580	24.580	24.570	0.011	3.6187
0	3	2	25.220	25.220	25.225	-0.005	3.5283
2	2	2	25.460	25.460	25.487	-0.0026	3.4956
2	0	3	26.060	26.060	26.051	0.010	3.4165
2	2	0	26.160	26.160	26.168	-0.008	3.4036
1	-3	0	26.320	26.320	26.335	-0.015	3.3833

TH (OBS) = 2θ observed TH (ZERO) = 2θ zero level TH (CALC) = 2θ calculated

L_2 crystallizes in the triclinic group and it has crystallographic parameters such as a = 7.9501 A^0, b = 18.3473 A^0 and c = 5. 8579A^0 α = 64.692^{o,} β = 98.068^o, γ =74.346^o. Its volume is 710.978 (A0)^3 and its minimum density is 2.961961 g\cm^3 .Calculated and measured h, k, l data is given in table no.3

Table No. 3 h, k, and l values of L_2

h	k	l	TH(OBS)	TH(ZERO)	TH(CALC)	DIFF	d value
1	2	1	20.340	20.285	20.293	-0.008	4.3625
1	4	1	22.660	22.605	22.598	0.007	3.9208
2	2	0	22.780	22.725	22.721	0.004	3.9004
2	3	0	24.140	24.085	24.085	0.000	3.6837
0	2	-1	25.360	25.305	25.306	0.000	3.5092
0	5	1	25.500	25.445	25.429	0.016	3.4902
1	5	1	25.780	25.725	25.724	0.001	3.4529
1	-4	-1	26.020	25.965	25.992	-0.027	3.4216
2	-1	-1	26.300	26.945	26.229	0.016	3.3858
2	4	0	26.720	26.665	26.683	-0.018	3.3336
1	5	0	26.960	26.905	26.898	0.007	3.3044
2	-1	0	27.080	27.025	27.018	0.007	3.2901
2	-2	-1	28.240	28.185	28.188	-0.003	3.1575

TH (OBS) = 2θ observed TH (ZERO) = 2θ zero level TH (CALC) = 2θ calculated

L3 crystallizes in the triclinic group and it has crystallographic parameters such as;

a = 7.1911 A^0, ^{b} = 17.6970 A^0 and c = 7.8654 A^0. α = 109.307^o, β = 66.704^o and γ = 7.8654^0.Its volume is 785.132(A0) and its minimum density is D min = 3.09429 g\cm^3. Calculated and measured values of h, k, l data is given in table no 4.

Table no 4 h, k, l values L_3

h	k	l	TH(OBS)	TH(ZERO)	TH(CALC)	DIFF	d value
1	2	-1	21.680	21.534	21.540	-0.006	4.0958
0	4	0	23.680	23.534	23.526	0.008	3.7542
1	4	-1	24.120	23.974	23.974	0.001	3.6867

0	2	-2	24.820	24.674	24.676	-0.002	3.5843
1	0	-1	25.320	25.174	25.173	0.001	3.5146
0	4	-2	26.840	26.694	26.692	0.002	3.3189
1	-4	1	27.400	27.254	27.258	-0.004	3.2524
2	3	1	27.600	27.454	27.449	0.005	3.2292
1	4	1	27.980	27.834	27.843	-0.009	3.1862
0	0	2	28.220	28.074	28.071	0.004	3.1597
2	0	2	28.640	28.494	28.495	-0.001	3.1143

TH (OBS) = 2θ observed TH (ZERO) = 2θ zero level TH (CALC) = 2θ calculated

L_4 crystallizes in the triclinic group and it has crystallographic parameters such as.
a = 10.9895 A^{0,} b = 8.7347 A^0 and c = 9.2280A^0 α = 82.733 ^{0}, β = 72.018^o and γ = 74.484 $^{o.}$ Its minimum density is Dmin = 3.220622 gm/cm^3. Calculated and measured values of h, k, l data is given in table no. 5

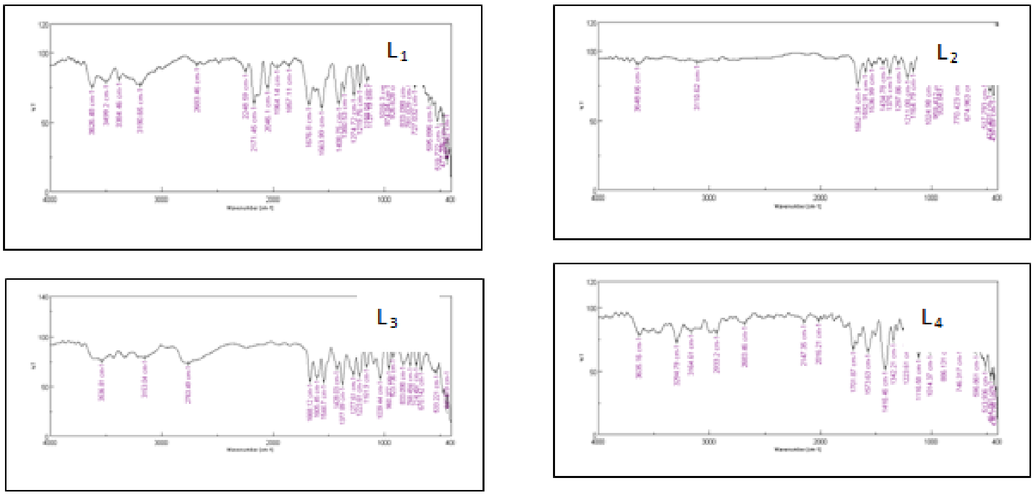
Table No.5 h,k.l values for L_4

h	k	l	TH(OBS)	TH(ZERO)	TH(CALC)	DIFF	d value
1	1	0	11.900	11.896	11.927	-0.031	7.4308
0	1	1	14.260	14.256	14.230	0.025	6.2059
1	0	-1	15.140	15.136	15.127	0.009	5.8471
1	1	2	20.760	20.756	20.756	0.000	4.2752
2	-1	1	22.780	22.776	22.786	-0.011	3.9004
2	1	-1	23.340	23.336	23.334	0.002	3.8081
1	-1	2	23.740	23.736	23.730	0.005	3.7448
2	2	0	24.000	23.996	23.985	0.011	3.7048
3	0	1	25.360	25.356	23.343	0.013	3.5092
2	-1	-1	26.580	26.576	26.576	-0.001	3.3508
1	-1	-2	27.000	26.996	27.011	-0.015	3.2996
3	1	2	27.500	27.496	27.502	-0.007	3.2408

TH (OBS) = 2θ observed TH (ZERO) = 2θ zero level TH (CALC) = 2θ calculated

3.2 Infra-Red Spectroscopy

Fig.2 shows IR frequencies of L_1,L_2,L_3 and L_4



IR spectra of L1, L2, L3 and L_4 were recorded in KBR matrix. Selected frequencies of bands such as N-H, C-H, C= IR are given in table no.6

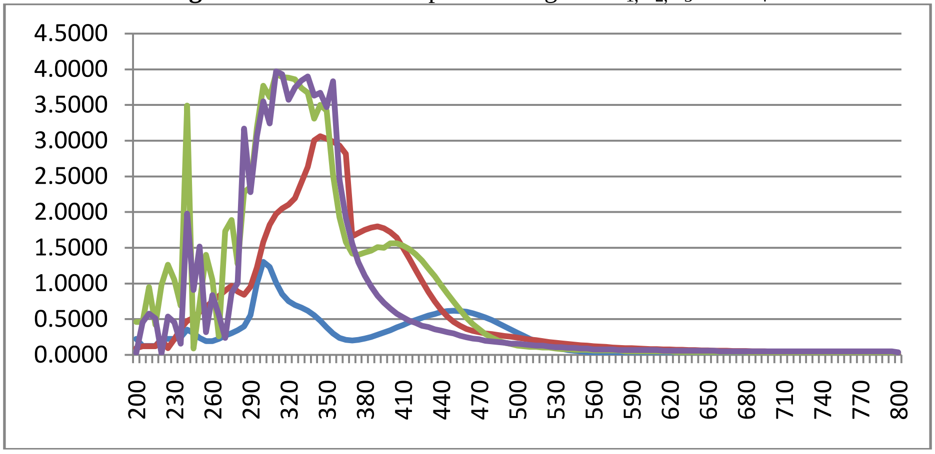
Table No. 6; IR bands of L_1, L2, L3 and L_4

Name	N-H BENDING	N - H STRECHING	C – N	C –H	C =O	C = C	C = O
L1	1563.99	3626.48	1274.72	3384.46	1676.8	781.029	
L2	1573.63	3635.16	1342.21	3294.79	1670.00	780.00	
L3	1605.45	3536.81	1277.61	3153.04	1668.12	768.494	670.142
L4	1592.91	3648.66	1297.86	3110.62	1662.34	770.423	674.963

Infra red spectra of 2-amino -1, 4-naphthoquinones have been fully discussed in the reported work. (17). Aromatic amines display strong CN stretching absorption in the 1342-1266 cm^{-1} region. The absorption appears at higher frequencies in to (wavelength) than the corresponding absorption of aliphatic amines because the force constant of the C-N bond is increase by resonance with the ring. The Infra red spectra of 2- amino -1,4 naphthoquinone as been fully discussed in the reported work characterization strong C-N stretching bonds in the spectra of aromatic amines have been assigned in the range 1340-1250cm^{-1}. The data for different stretching and bending vibration of this compound are reported for N-H, C-H, C=O, C= N, N-O and OH. All the frequencies are compared to the literature values. The frequencies are C=H, C=O, C=N are matching to the reported values (18). The frequencies of OH and CN matching to their reported values (19).

3.3 Electronic Spectra:

Fig.3 Shows electronic spectra of ligand L_1,L_2,L_3 and L_4



L_1= Blue, L_2 = Red, L_3 = Green and L_4 = Purple

Table no. 7 – Electronic spectra of ligand L_1,L_2,L_3 and L_4 in DMSO

Compound	λ$Max_{1\ nm}$	λ$Max_{2\ nm}$	λ$Max_{3\ nm}$
L_1	275.0	345.0	390.0
L_2	240.0	-	300.0
L_3	215.5	315.5	331.0
L_4	279.0	310.5	350.5

The electronic spectrum is determined in DMSO solvent. L_1 spectrum shows 3 peaks at 275 nm, 345 nm & 390 nm. First peak is assigned as $\pi - \pi^*$ which is also known as benzenoide electronic transition. Second pick is π-π^* which is generally assigned as quinonoid electronic transition and the third peak is due to n-π^* which is also known as charged transition. L_2 ligand shows only 2 peaks, first at 240nm and second at 300nm. We do not observe benzenoide transition but first peak is due to quinonoide transition. The peak at 300nm is due to n-π^* . It is associated with the intra molecular ligand charged resonance (20) . ligand L3 gives 3 bands at 215.5nm , 315.5nm & 331nm and the assignments are similar to ligand L1 . ligand L4 gives 3 bands at 279nm , 310.5nm & 350.5nm . First band is due to benzene electronic transition i.e. π-π^* . the second peak is for QET which is due to π-π^* transition. Third band of n-π^* transition show bathochromic effect at 350.5 nm (21).

III. Conclusion

The x-ray diffraction shows that the ligands are crystalline in nature . All ligands belongs to triclinic group. The wave numbers of Infra red spectra wave compared with reported values & found to be good relation .Electronic transition are observed for π-π* & n-π*. These values are closed matching to the reported work. Bathochromic effect is observed for n-π^* transition .These are useful as pharmaceutical chemicals.

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