Synthesis, Characterization and DFT Study of 2,5-bis(2-carboxyphenylamino)-3,6-dichloro-1, 4-benzoquinone

Kumar Rakesh Ranjan[1] and Damini Sharma[2]

[1,2]Amity Institute of Applied Sciences Amity University, Sec-125, Noida
E-mail: [1]krranjan@amity.edu, [2]damini.sharma208@gmail.com

Abstract—*To investigate the effect of distance between two metal centers on the magnetic exchange coupling, a novel ligand 2,5-bis(2-carboxyphenylamino)-3,6-dichloro-1,4-benzoquinone has been synthesized and characterized. DFT calculation was performed on the ligand to optimize the structure, to solve NMR and IR spectrum. Synthesis, characterization and study of properties of metal complexes are under investigation.*

Keywords*: - ligand, DFT calculation, optimize, metal complexes.*

1. INTRODUCTION

The degree of communication between the different metal centers is the most interesting aspect in the study of the chemistry of such multinuclear complexes. The magnitude of the metal-metal interaction is largely contributed by all the three basic units of the polynuclear assemblies viz. the metal ion, the bridging ligand and the terminal ligands. In order to evaluate the influence of the above mentioned three basic units on the degree of communication between the metal centers, a plethora of studies on novel ligand has been carried out [1-2].

Keeping these points in view and role of extensive π-delocalized ligand to propagate the magnetic coupling [3-5], we have synthesized and characterized 2,5-bis(2-carboxyphenylamino)-3,6-dichloro-1,4-benzoquinone. The results of the studies are reported in this paper.

2. EXPERIMENTAL DETAILS

2.1 Materials

The chemicals such as 2-aminobenzoic acid (Aldrich, USA), p-chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone), (Himedia, India) were used as obtained.

Synthesis of 2,5-bis(2-carboxyphenylamino)-3,6-dichloro-1,4-benzoquinone

Ligand was prepared by adding 2-aminobenzoic acid (0.274gm., 2 mmol) to the suspension of p-chloranil (0.246g, 1 mmol) in ethanol (10 ml). The reaction mixture was stirred at 65 °C for 12 h, which yielded a dark brown precipitate. The precipitate was filtered and washed with acetone (4-5 times) to remove any traces of the unreacted reagent. The vacuum dried powder (brown, 73% based on p-chloranil, decomposes at ~ 283 °C) is taken for further characterization.

2.2 Physical Measurements

Elemental analyses were performed on a CE-440 Exeter Analytical CHN analyzer. Infrared spectra were recorded on Varian 300 FT-IR Excalibur spectrophotometer from 4000 to 400 cm^{-1} (KBr). ^{1}H and ^{13}C NMR spectra in DMSO-d$_6$ were obtained on a JEOL FT NMR AL 300 MHz spectrometer using tetramethylsilane (TMS) as the internal standard.

2.2 Computational details

Calculations of structural parameters, atomic charges and vibrational frequencies of the ligand molecule were carried out on a Pentium IV, PC using window version of Gaussian 03 suite of *ab initio* quantum chemical program. Initially, the geometry optimization and calculation of other parameters were performed at restricted Hartree–Fock (RHF) level using 6–31+G* basis set. Electron correlations were included using Becke3–Lee–Yang–Parr (B3LYP) procedure [6-8]. This includes Becke's gradient exchange corrections, Lee, Yang and Parr correlation functions and / or Vosko, Wilk and Nusair correlation functions [9]. The optimized geometry at RHF/6–31+G* level was taken as the input structure for the density functional calculation at B3LYP/6-311+G* level. Finally, the optimized geometry at the B3LYP/6-31+G* level was used as starting geometry for calculation at the B3LYP/6-311++G** level. No symmetry constraints were applied in optimizing geometry. The experimentally observed vibrational frequencies are assigned by the help of Gview. The calculated value of vibrational frequencies (from Gaussian) may vary by 4.5% from the experimental value. This is the expected range of agreement for the B3LYP density functional theory [10].

3. RESULTS AND DISCUSSIONS

The compound 2,5-bis(2-carboxyphenylamino)-3,6-dichloro-1,4-benzoquinone (Fig. 1) have been prepared. The elemental data confirms the formation of the compounds. The physical data i.e. yield (%), the carbon, hydrogen, nitrogen and the metal contents of the complexes are summarized in Table 1.

Table 1: Analytical data and % yield of the ligand

Complex	Formula wt.	Yield (%)	Found (calcd. %)		
			C	H	N
$C_{20}H_{12}N_2O_6Cl_2$	447.23	73	53.23 (53.71)	3.01 (2.70)	5.99 (6.26)
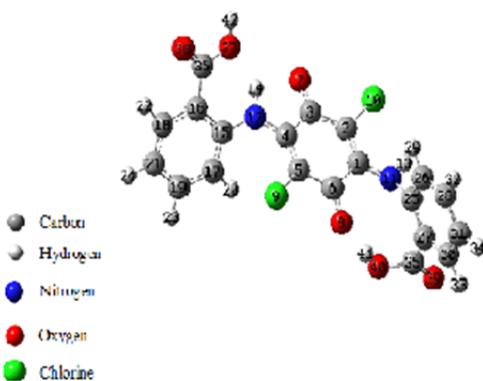
Fig. 1: Optimized molecular structure of 2,5-bis(2-carboxyphenylamino)-3,6- dichloro-1,4 -benzoquinone (numbering is not as per the IUPAC nomenclatur

3.1 Infrared Spectral Studies

The spectrum of ligand is assigned with the help of vibrational output of the Gaussian result (See Table 2). The bands (Fig. 2) in the 3450–3000 cm^{-1} region comprise the bands due to –OH, –NH and aromatic C–H stretchings. The bands around 1675, 1601, 1511, 1266, 900 and 581 cm^{-1} are attributed to ν(C=O) quinone, ν(C=C) quinone, ν(C–N), ρ(N–H), ν(C–Cl) and ω(O–H), respectively.
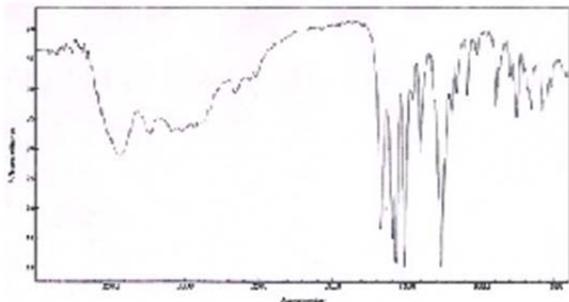
Fig. 2: Mid IR spectrum of ligand

Table 2: Calculated and experimental IR frequencies (cm^{-1}) for ligand

Calculated Frequencies B3LYP/6-311++G**	Experimental [a]	Assignments
430.775	421.0	Φ + ω (N-H)
584.119	581.774	ω (O-H)
674.348	658.817	ω (N-H)
722.317	705.470	Φ
786.175	758.230	ω (C-H) + ω (O-H)
814.744	802.968	ω (O-H) + ω (C-H)
906.607	898.082	ν (C-Cl) + ρ (C-N) + Φ + ω (C-H)
1103.7	1089.421	α + ν (C-O) + ρ (C-H)
1141.96	1166.791	ρ (C-H) + ν (ring) + ν (C-O)
1207.5	1199.491	ρ (O-H) + ρ (C-H) + ν (C-N) + δ (ring)
1248.89	1266.414	ρ (N-H) + ν (C-C) + ρ (C-H) + ν (C-O) + ρ (O-H)
1304.77	1298.244	ρ (C-H) + ν (C-C) + ρ (O-H)
1324.86	1318.040	ν (C-C) + ν (C-N) + ρ (C-H) + ρ (O-H)
1382.37	1410.800	ρ (O-H) + ν (C-O) + ν (C-N)
1481.89	1456.605	ρ (C-H) + ν (C-C) + ν (C-N)
1515.73	1511.162	ν (C-N) + ν (C-C) + ρ (C-H)
1565.42	1571.495	ρ (N-H) + ν (C-N) + ν (C-C) + ρ (C-H)
1601.09	1601.792	ν (C=C) + ν (C-N) + ρ (N-H) + ν (C-C)
1681.12	1675.435	ν (C=O, quinone) + ν (C-N)
3181.07	3017.230	ν (C-H, assym.)
3199.9	3078.120	ν (C-H, sym.)
3472.9	3227.920	ν (N-H) + ν (O-H)
3761.36	3430.791	ν (O-H)

[a] from solid state vibrational spectra in KBr pellet

Φ = non − planar ring deformation, α = planar ring deformation, π = out-of-plane deformation,　ν = stretching, ω = wagging, ρ = rocking, δ = angle-bending or deformation and τ = twisting

3.2 NMR Spectral Studies

^{1}H NMR spectrum (Fig. 3a) displays peaks at δ (ppm) (DMSO,TMS): 13.483 (s, 2H, acidic), 10.183 (s, 2H, NH), 7.906-7.584 (d, 4H, ArH), 7.225-7.040 (d, 4H,ArH). These are assigned with the help of Mulliken charge on particular atom to the pairs (H[41],H[42]); (H[13],H[14]); (H[22],H[33]); (H[20],H[29]); (H[23],H[32]) and (H[24],H[34]), respectively. ^{13}C NMR (DMSO) The ^{13}C NMR spectrum (Fig. 3 b) displays peaks at δ (ppm) (DMSO, TMS): 174.185 (s, 2C, C=O quinonic), 168.358 (s, 2C, C=O acidic), 141.474 (s, 2C, C$_{quinonic}$-N), 138.218, 132.062, 130.628, 124.034, 121.043 (Aromatic), 107.798 (s, 2C, C-Cl). These are assigned with the help of Mulliken charge on particular atom to the pairs (C3,C6); (C35,C36); (C1,C4); (C16,C27); (C15,C25); (C18,C30); (C19,C28); (C17,C26); (C21,C31) and (C2,C5), respectively.

Fig. 3: ^{1}H NMR spectrum (a) and ^{13}C NMR spectrum (b)

4. CONCLUSION

A novel ligand 2,5-bis(2-carboxyphenylamino)-3,6-dichloro-1,4-benzoquinone has been synthesized and characterised through NMR and IR spectroscopy. The optimised geometry is obtained by DFT calculation. The mulliken charge on Hydrogen and Carbon helps in determining the position in NMR signal. The calculated vibrational frequency is in good agreement with the experimental one.

REFERENCE

[1] S. Serroni, S. Campagna, F. Puntoriero, C.D.Pietro, N.D. McClenaghan, F. Loiseau. Chem. Soc. Rev., 367 (2001).

[2] J.-P. Launay. Chem. Soc. Rev., 386 (2001).

[3] T.R. Felthouse; E.N. Duesler, A.T. Christenson, D.N. Hendrickson. Inorg. Chem., 18, 245 (1979).

[4] T.R. Felthouse, D.N. Hendrickson. Inorg. Chem., 17, 2636 (1978).

[5] E.F. Hasty, T.J. Colburn, D.N. Hendrickson Inorg. Chem., 12, 2414 (1973).

[6] Becke A.D., Density-functional thermochemistry. The role of exact exchange, J. Chem. Phys., 8, 5648-5652(1993).

[7] Lee, C., Yang, W., Parr, R.G., Development of the collle-salvetti correlation energy formula into a functional of the electron density, Phys. Rev. B, 37, 785-789 (1998).

[8] Becke, A.D., Density-functional exchange-energy approximation with correct asymptotic behavior, Phys. Rev. A, 38, 3098-3100 (1998).

[9] Vosko, S.H., Wilk, L., Nusair, M., Accurate spin-depemdent electron-liquid correrelation energies for local density calculations: a critical analysis, Can.J. Phys., 58, 1200-1211 (1980).

[10] Wang, X., Andrews, L., Infrared Spectra of $M(OH)_{1,2,3}$ (M=Mn, Fe, Co, Ni) Molecules in solid Argon and the character of first row Transition Metal Hydroxide Bonding, J. Phys. Chem. A, 110, 10035-10045 (2006).