MOLECULAR STRUCTURE, SPECTROSCOPIC INVESTIGATION, NONLINEAR OPTICAL AND OTHER MOLECULAR PROPERTIES OF 2,3-DICHLORO-1,4-NAPHTHOQUINONE

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ABSTRACT

The FT-Raman (3500 – 50 cm⁻¹) and FT-IR (4000-400 cm⁻¹) spectra of 2,3-dichloro-1,4-naphthoquinone (DCNQ) were recorded and complete vibrational assignment and analysis of the fundamental modes were carried out. Subsequently, these were confirmed by total energy distribution (TEDs). Calculations were performed by using the density functional theory (DFT/B3LYP) method with 6-31+G(d,p) and 6-311++G(d,p) basis sets, and the optimum molecular geometry, harmonic vibrational frequencies, infrared intensities and Raman scattering activities were determined. Comparison of the results with experimental values showed only a very small difference between the observed and scaled wavenumber values of most of the vibrational modes. The NLO properties such as polarizability and first hyperpolarizability of the molecule have been calculated. The effects of frontier orbitals, HOMO - LUMO and the transition of electron density transfer have been discussed. The theoretical UV-Vis spectrum has been done which confirms the charge transfer of DCNQ. Natural bond orbital (NBO) analysis was used for the chemical interpretation of hyperconjugative interactions and charge delocalization. Further, the thermodynamic, Mulliken's charge and molecular electrostatic potential (MEP) analyses have been computed.

Keywords: FTIR, FT-Raman, DFT, 2,3-dichloro-1,4-naphthoquinone, NLO, NBO

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INTRODUCTION

The biological activities of compounds containing quinone groups find active agents against many diseases and the electron donor-acceptor phenomena of quinones were studied due to their potential non-linear optical activity. By the introduction of chloro, cyano groups with naphthoquinones, the electron affinity properties were enhanced^{1,2}. Recently, the antifungal and anti-bacterial activity of the nucleophilic substitution reactions of 1,4- naphthoquinone derivatives has been studied³. Moreover, the biological evaluation, antioxidant and cytotoxic activity of substituted 1,4-naphtho and benzoquinones have been investigated⁴. Further, the electron attracting and donor accepting property of the quinone affected the redox properties and modulated it which is responsible for the oxidative stress⁵. More recently, the electrophilicity of the naphthaquinone can be increased by the substitution reactions due to the intramolecular bond formation between the terminal groups⁶. In the same way, the title compound 2,3-dichloro-1,4-naphthoquinone (DCNQ) has many special properties and some unique characters because of the structure of quinone, which are naturally found in many derivatives. Hence, in the present investigation, molecular geometry, optimized parameters and vibrational frequencies of DCNQ are computed and the performance of the computational method for B3LYP with the standard 6-31+G(d,p)

and 6-311++G(d,p) basis sets are compared. Relatively accurate molecular structure and vibrational spectra are predicted by these methods.

EXPERIMENTAL

The spectroscopic grade compound DCNQ was purchased from Lancaster Chemical Company, UK and is used as such, without further purification, for recording the spectra. A Perkin Elmer FTIR spectrometer equipped with an MCT detector, a KBr beam splitter and globar source, was used to record the FTIR spectrum ($4000 - 400 \text{ cm}^{-1}$) of the compound. The spectral resolution is $\pm 1 \text{ cm}^{-1}$. The FT-Raman spectrum of the title compound have been recorded in the Stokes region ($3500 - 50 \text{ cm}^{-1}$) on a computer interfaced BRUKER RFS-66V model interferometer using Nd: YAG laser source operating at 1064 nm excitation wavelength, line width with 200 mW power. The frequencies of all sharp bands are accurate to $\pm 1 \text{ cm}^{-1}$.

DFT Calculations

Quantum chemical density functional calculations were carried out for DCNQ with the 2009 Window version of the GAUSSIAN suite program⁷ using Becke-3-Lee-Yang-Parr (B3LYP) functional^{8,9} supplemented with the standard 6-31+G(d,p) and 6-311++G(d,p) basis sets. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true energy minimum, as revealed by the lack of imaginary values in the wave number calculations. The Cartesian representation of the theoretical force constants has been computed at the fully optimized geometry by assuming the molecule belongs to C_{2v} point group symmetry. A PC with the version V7.0-G77 of the MOLVIB program written by Sundius¹⁰, was used for the transformation of force field from Cartesian to internal local-symmetry coordinates, the scaling and calculation of total energy distribution (TED).

RESULTS AND DISCUSSION

Molecular Geometry

The molecular structure of DCNQ is shown in Fig.-1. The title molecule contains chlorine and oxygen atoms attached with the pair of benzene rings fused together.

Fig.-1: Molecular Model of 2,3-Dichloro-1,4-Naphthoquinone along with Numbering of Atoms.

Figs.-2 and 3 show the experimental and calculated FTIR and FT-Raman spectra of DCNQ, respectively. The comparative optimized structural parameters such as bond lengths and bond angles of DCNQ are

presented in Table-1. Most of the theoretically estimated bond lengths are found to be slightly larger than the experimental values, due to the obvious reason that the calculations are done for individual molecules without considering the solid state effects¹¹. Other parameters, such as vibrational frequencies and thermodynamic properties, were estimated using the calculated geometrical parameters as the base. The global minimum energy obtained by the DFT structure optimization with the 6-31+G(d,p) and 6-311++G(d,p) basis sets for DCNQ is calculated as -1454.23632159 and -1454.40258930 Hartrees, respectively.

Fig.-2: Comparison of Observed and Calculated IR Spectra of 2,3-Dichloro-1,4-Naphthoquinone (a) Observed; (b) Calculated with B3LYP/6-311++G(d,p); and (c) Calculated with B3LYP/6-31+G(d,p).

The substitutions of chlorine and oxygen atoms in the place of H atoms make the fused rings appear little distorted and angle slightly out of the perfect planar structure. According to the experimental values of the molecule¹², the order of the optimized bond length of the C–C bonds of the ring are as C2–C3 < C6–C7 < C7–C8 < C5–C10 < C8–C9 < C9–C10 < C5–C6 < C1–C9 < C3–C4 < C4–C10 < C1–C2. But, as per the calculated values (B3LYP/6-311++G (d,p)), the order of the bond lengths is slightly differed as C2–C3 < C5–C6 = C7–C8 < C6–C7 < C5–C10 = C8–C9 < C9–C10 < C4–C10 = C1–C9 < C1–C2 = C3–C4, since the phases are different. The fused ring system appears to be distorted with both the bond lengths C1–C2 and C3–C4 exactly at the substitution place are calculated as 1.502 Å, longer than remaining bonds (~1.352 Å to ~1.488 Å by the cal.) in the ring. Also, the C–Cl bond lengths indicate a considerable increase when substituted in place of C–H. The C2–Cl12 and C3–Cl13 bond lengths are found to be 1.724 Å by B3LYP/6-311++G (d,p), which are 0.005 and 0.003 Å smaller and larger than the experimental value (1.699 and 1.727 Å), respectively. The changes in charge distribution on the carbon atoms of the ring on substitution with chlorine and oxygen atoms are responsible for the changes in the bond length and breakdown of regular hexagonal symmetry of the ring. According to the DFT calculations, both the bond angles C1–C2–C3 and C2–C3–C4 is increased by 1.89° from 120°, at the C2 and C3 positions and this asymmetry of the exocyclic angles reveal the repulsion between chlorine atoms and the fused ring system. The bond angles C2–C1–C9 and C3–C4–C10 also show the asymmetry of the benzene ring, where the oxygen atoms are attached at C1 and C4 carbon atoms.

Table-1: Optimized Geometrical Parameters for 2,3-Dichloro-1,4-Naphthoquinone

Bond length	Value (Å)		^a Experimental	Bond angle	Value (°)		^a Experimental
	B3LYP/6-31+G(d,p)	B3LYP/6-311++G(d,p)			B3LYP/6-31+G(d,p)	B3LYP/6-311++G(d,p)	
C1-C2	1.503	1.502	1.518	C2-C1-C9	117.21	117.05	117.1
C1-C9	1.490	1.488	1.469	C2-C1-O11	120.71	120.77	119.8
C1-O11	1.221	1.213	1.205	C9-C1-O11	122.09	122.18	123.1
C2-C3	1.356	1.352	1.313	C1-C2-C3	121.80	121.89	120.0
C2-Cl12	1.725	1.724	1.699	C1-C2-Cl12	115.55	115.44	115.3
C3-C4	1.503	1.502	1.483	C3-C2-Cl12	122.65	122.67	124.6
C3-Cl13	1.725	1.724	1.727	C2-C3-C4	121.80	121.89	125.0
C4-C10	1.490	1.488	1.500	C2-C3-Cl13	122.65	122.67	120.7
C4-O14	1.221	1.213	1.197	C4-C3-Cl13	115.55	115.44	114.3
C5-C6	1.395	1.391	1.411	C3-C4-C10	117.21	117.05	115.7
C5-C10	1.399	1.397	1.382	C3-C4-O14	120.71	120.77	122.2
C5-H15	1.085	1.083	-	C10-C4-O14	122.71	122.18	122.0
C6-C7	1.400	1.396	1.359	C6-C5-C10	119.90	119.92	118.8
C6-H16	1.086	1.084	-	C6-C5-H15	121.37	121.34	-
C7-C8	1.395	1.391	1.380	C10-C5-H15	118.73	118.74	-

C7-H17	1.086	1.084	-	C5-C6-C7	120.18	120.18	119.8
C8-C9	1.399	1.397	1.384	C5-C6-H16	119.77	119.80	-
C8-H18	1.085	1.083	-	C7-C6-H16	120.05	120.01	-
C9-C10	1.406	1.403	1.393	C6-C7-C8	119.77	120.18	121.2
				C6-C7-H17	117.21	117.05	-
				O8-C7-H17	120.71	120.77	-
				C7-C8-C9	122.09	122.18	120.1
				C7-C8-H18	121.80	121.89	-
				C9-C8-H18	115.55	115.44	-
				C1-C9-C8	122.65	122.67	119.0
				C1-C9-C10	121.80	121.89	121.9
				C8-C9-C10	122.65	122.67	119.1
				C4-C10-C5	115.55	115.44	118.8
				C4-C10-C9	117.21	117.05	120.2
				C5-C10-C9	120.71	120.77	121.0

^aExperimental Values (Ref. 12.)

Fig.-3: Comparison of Observed and Calculated Raman Spectra of 2,3-Dichloro-1,4-Naphthoquinone (a) Observed; (b) Calculated with B3LYP/6-311++G(d,p); and (c) Calculated with B3LYP/6-31+G(d,p)

Vibrational Assignment

As the DCNQ consists of 18 atoms, there are 48 normal modes of vibrations, in agreement with C_{2v} point group symmetry. All the fundamental vibrations are active in both Raman scattering and IR absorption. The detailed vibrational assignment of fundamental modes of DCNQ along with the calculated IR and Raman frequencies and normal mode descriptions (characterized by TED) are reported in Table-2.

The assignment of the observed frequencies to different vibrational modes can be made easy with the help of a reliable prediction of vibrational spectra by computational methods. The selection of adequate quantum chemical methods and scaling procedures remarkably reduces the risk in the assignment and can accurately determine the contribution of the different modes in an observed band. DFT calculations were reported to provide excellent vibrational frequencies of organic molecules if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlations, for basis set deficiencies, and for anharmonicity. The possible errors in the DFT calculations due to the approximate treatment of electron correlations, basis set deficiencies and anharmonicity can be compensated by proper scaling of frequencies estimated by DFT calculations, and excellent vibrational frequencies of organic molecules can be provided. A number of studies have been carried out regarding the calculations of vibrational spectra using B3LYP method with the 6-31+G(d,p) and 6-311++G(d,p) basis sets, which has helped us in very accurately interpreting the observed vibrational frequencies and IR intensities. The scaling factor was applied successfully to the B3LYP method and found to be easily transferable to a number of molecules¹³. Therefore, the calculated wavenumbers were scaled by using a scaling factor of 0.9613 for B3LYP method¹⁴. The analyses for the vibrational modes of DCNQ were presented in some detail in order to describe the basis for the assignments.

C-H Vibrations

The C-H stretching vibrations of benzene derivatives¹⁵ generally appear in the region 3100 – 3000 cm^{-1} . In this region, the bands are not affected appreciably by the nature of the substituents. Hence, in this study, the FTIR band found at 3180, 3125, 3100, and 3025 cm^{-1} and the Raman band at 3100, 3020 cm^{-1} are assigned to C-H stretching vibrations, which are confirmed by their TED values. The sharp bands, observed in the region 1300 – 1000 cm^{-1} , are due to C-H in-plane bending vibrations. The C-H out-of-plane bending vibrations are strongly coupled. The C-H in-plane bending vibrations of DCNQ are observed at 1282, 1230, 1202, 1150 cm^{-1} in IR, and at observed at 1280, 1238, 1195, 1158 cm^{-1} in Raman. From Table 2 it can be seen that, for C-H vibrational modes, the theoretically computed values (B3LYP/6-311++G(d,p) method) and the experimental data are in excellent agreement.

C=O Vibrations

The vibrational frequencies of the carbonyl group have been the subject of extensive studies because they are the significant characteristic bands in the vibrational spectra of ketones¹⁶. The IR and Raman bands of these vibrations are of high intensity due to conjugation. The stretching vibrations of carbonyl in ketones, which are expected in the region 1680–1715 cm^{-1} , are observed at 1690, 1625 cm^{-1} in both IR and Raman spectra. The bands at 680 cm^{-1} in IR and 632 cm^{-1} in Raman are assigned to C=O in-plane bending vibrations for DCNQ, which are in agreement with similar reports in literature¹⁶.

C-Cl Vibrations

The lowering of molecular symmetry and the presence of heavy atoms on the periphery of molecules leads to mixing of vibrations belonging to the bond between the ring and halogen atoms. Generally, the C-Cl absorption is obtained in the broad region¹⁷ between 850 and 550 cm^{-1} . For DCNQ, the strong bands found at 800, 784 cm^{-1} in IR and 800 cm^{-1} in the Raman have been designated to C-Cl stretching modes of vibration and the corresponding force constant contribute nearly 75% to the TED. In the case of most of the aromatic chlorine compounds, the C-Cl in-plane bending vibration gives rise to strong to medium intensity bands in the region 385-265 cm^{-1} . Accordingly, in this study, the bands identified at 480 cm^{-1} in FTIR and 480, 410 cm^{-1} in the Raman have been assigned to the C-Cl in-plane bending modes of DCNQ. The C-Cl out-of-plane deformations for DCNQ have been established at 241 and 190 cm^{-1} in the Raman spectrum. These are in good agreement with the literature data¹⁷.

C-C Vibrations

The bands between 1430 and 1625 cm^{-1} in benzene derivatives are due to C-C stretching vibrations¹⁸. Therefore, the C-C stretching vibrations of DCNQ are found at 1612, 1584, 1545, 1530, 1482, 1475, 1424, 1400, 1380, 1364 cm^{-1} in the FTIR and 1572 cm^{-1} in the FT-Raman spectrum. These normal modes are confirmed by their TED values. Most of the ring vibrational modes are affected by the substitutions in the aromatic ring of DCNQ. The C-C-C in-plane bending bands¹⁹ always occur between the range 1000–600 cm^{-1} . In the present study, by careful consideration of their quantitative descriptions, the Raman bands observed at 1320, 1308, 1298, 1130, 1100 in IR and 1300, 1100, 1050 cm^{-1} , are assigned to ring in-plane bending modes. The higher percentage of TED obtained for this group encouraging and confirms the assignments proposed in this study for ring in-plane bending vibrations of DCNQ. The ring out-of-plane bending modes of DCNQ are also listed in Table-2.

Vibrational Contribution to NLO Activity and First Hyperpolarizability

Non-linear optical properties of molecular crystals have paid much attention to both practical and theoretical reasons. The title compound has potential application in the field of nonlinear optics. This makes it necessary that a thorough investigation of its structural and bonding features contributing to the hyperpolarizability enhancement, has to be carried out by analyzing the vibrational modes using IR and Raman spectroscopy. The first hyperpolarizability (β) of this molecular system is calculated using the B3LYP/6-311++G(d,p) method, based on the finite field approach. When a system is placed in an electric field, its energy becomes a function of the applied field. The first hyperpolarizability can be described by a $3 \times 3 \times 3$ matrix, a third-rank tensor, the 27 components of which can be reduced to 10 components, using Kleinman symmetry²⁰.

The components of β are the coefficients in the Taylor series expansion of the energy in the external electric field. For a weak and homogeneous electric field, this expansion becomes:

$$E = E_0 - \sum_i \mu_i F^i - \frac{1}{2} \sum_{ij} \alpha_{ij} F^i F^j - \frac{1}{6} \sum_{ijk} \beta_{ijk} F^i F^j F^k - \frac{1}{24} \sum_{ijkl} \nu_{ijkl} F^i F^j F^k F^l + \dots$$

Where, E_0 is the energy of the unperturbed molecule; F^i is the field at the origin; and μ_i , α_{ij} , β_{ijk} and ν_{ijkl} are the components of dipole moment, polarizability, the first hyper-polarizabilities and second hyper-polarizabilities, respectively. The total static dipole moment μ , the mean polarizability α_0 and the mean first hyperpolarizability β_0 , using the x, y, z components are defined as follows,

$$\begin{aligned} \mu &= \left(\mu_x^2 + \mu_y^2 + \mu_z^2 \right)^{1/2} \\ \bar{\alpha} &= \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \\ \Delta\alpha &= \frac{1}{\sqrt{2}} \left[\left(\alpha_{xx} - \alpha_{yy} \right)^2 + \left(\alpha_{yy} - \alpha_{zz} \right)^2 + \left(\alpha_{zz} - \alpha_{xx} \right)^2 + 6\alpha_{xx}^2 \right]^{1/2} \\ \beta &= \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz} \right)^2 + \left(\beta_{yyy} + \beta_{xxy} + \beta_{yzz} \right)^2 + \left(\beta_{zzz} + \beta_{xxz} + \beta_{yyz} \right)^2 \right]^{1/2} \end{aligned}$$

The calculated values of total static dipole moment μ , the average linear polarizability $\bar{\alpha}$, the anisotropy of the polarizability $\Delta\alpha$, and the first hyperpolarizability β using the DFT-B3LYP/6-311++G(d,p) method are 3.8577 Debye, 24.525 $\text{\AA}^3$, 20.843 $\text{\AA}^3$ and $3.246 \times 10^{-30} \text{ cm}^5 \text{ e.s.u.}^{-1}$, respectively. Urea, which is one of the prototypical molecules used in the study of the NLO properties of molecular systems, is commonly used as a threshold value for comparison. The values of μ , $\bar{\alpha}$ and β obtained by Sun *et al.*²¹ with the B3LYP/6-311++G(d,p) method for urea are 1.373 Debye, 3.831 $\text{\AA}^3$ and $0.3729 \times 10^{-30} \text{ cm}^5 \text{ e.s.u.}^{-1}$, respectively. The first hyperpolarizability of the title compound is 9 times greater than that of urea. The magnitude of the first hyperpolarizability value of the present compound indicates the use of it as a potential candidate for the development of NLO materials.

Thermodynamic Properties

Table-3 shows the standard thermodynamic functions such as heat capacity (C), entropy (S) and dipole moment (μ) of the title compound, obtained from theoretical harmonic frequencies. The values calculated by both the basis sets are only marginally different. The specific heat and rotational constants are increasing, from lower to higher basis sets for B3LYP. The same trends have been observed in entropy calculations. As the magnitude of the dipole moment is strongly related to structural stability, the prediction of its accurate value is very important. If the structural stability is high, the dipole moment is lower. In the present study, the total dipole moment of DCNQ determined by B3LYP method using 6-31+G(d,p) and 6-311++G(d,p) basis sets is 3.9308 and 3.8577 Debye, respectively. The structural stability of the title compound, at B3LYP/6-311++G(d,p) level, is high as its dipole moment, at B3LYP/6-31+G(d,p), is lower than one. We have presented the total energy of the title compound and its change in total entropy, at room temperature. All the thermodynamic data give helpful information for the further study of the title molecule and they can be used to compute other thermodynamic energies and estimating the directions of chemical reactions²².

Table-2: Vibrational Assignments of Fundamental Modes of 2,3-Dichloro-1,4-Naphthoquinone along with Calculated IR Intensity (km/mol), Raman Activity ($\text{\AA} \text{ amu}^{-1}$) and Normal Mode Descriptions (Characterized by TED) Based on Quantum Mechanical Calculations using DFT Method

Observed Wavenumber (cm ⁻¹)		Calculated frequencies (cm ⁻¹)								TED% among Types of Coordinates
		B3LYP/6-31+G(d,p)				B3LYP/6-311++G(d,p)				
FTIR	FT Raman	Unscaled	Scaled	IR intensity	Raman activity	Unscaled	Scaled	IR intensity	Raman activity	
3180(w)	3100(w)	3369	3239	6.04	214.96	3331	3202	5.34	214.04	vCH(98)
3125(vw)	-	3366	3236	1.79	39.98	3328	3199	2.12	39.67	vCH(96)
3100(ms)	-	3357	3227	3.88	135.71	3318	3190	3.08	128.34	vCH(94)
3025(w)	3020(vw)	3346	3217	3.63	67.85	3307	3179	3.41	63.97	vCH(98)
1690(vs)	1690(s)	1648	1584	5118.00	198.09	1628	1565	0.63	192.51	vC=O(89)
1625(s)	1625(ms)	1637	1574	82.12	18.22	1616	1553	74.14	21.03	vC=O(85)
1612(w)	-	1608	1546	119.28	15.79	1588	1527	175.90	14.45	vCC(82)
1584(w)	-	1566	1505	77.85	13.54	1549	1489	77.31	14.45	vCC(84)
-	1572(ms)	1502	1444	140.85	158.63	1485	1428	155.46	136.06	vCC(83)
1545(vs)	-	1445	1389	10.41	42.51	1436	1380	8.90	42.01	vCC(80)
1530(vs)	-	1397	1343	183.46	183.46	1380	1327	9.12	214.43	vCC(84)
1482(ms)	-	1369	1316	24.19	24.19	1339	1287	7.66	12.65	vCC(81)
1475(vw)	-	1304	1254	155.90	28.43	1292	1242	150.14	30.80	vCC(82)
1424(vw)	-	1257	1208	5.76	0.21	1255	1206	10.21	0.76	vCC(84)
1400(vw)	-	1216	1169	105.92	159.25	1203	1156	105.73	148.99	vCC(83)
1380(ms)	-	1152	1107	1.98	14.35	1152	1107	2.83	13.88	vCC(80)
1364(ms)	-	1116	1073	0.60	1.32	1112	1069	0.65	1.82	vCC(80)
1320(w)	-	1039	999	0.18	46.91	1032	992	0.01	51.24	R1 symd (76)
1308(s)	1300(w)	968	931	0.00	0.09	974	936	0.00	0.16	R1 trigd (74)
1298(vs)	-	968	931	3.50	8.74	969	931	2.07	0.11	R1 asymd (76)
1282(ms)	1280(w)	958	921	1.87	0.10	960	923	3.97	8.40	bCH(76)
1230(w)	1238(vw)	910	875	21.35	1.52	909	874	21.64	2.10	bCH(78)
1202(w)	1195(w)	907	872	24.22	58.44	892	857	30.45	45.46	bCH(76)
1150(vs)	1158(vw)	860	827	0.00	0.03	865	832	0.00	0.01	bCH(74)
1130(vs)	-	767	737	67.89	156.75	762	733	3.43	0.07	R2 symd (76)
1100(w)	1100(w)	758	729	0.59	0.38	751	722	65.81	160.14	R2 trigd (74)
-	1050(ms)	726	698	0.00	0.14	724	696	0.00	0.30	R2 asymd (76)
1025(vw)	-	697	670	132.80	0.05	687	660	3.43	1.29	ω CH (67)
-	900(vw)	680	654	0.00	0.30	684	658	65.81	0.30	ω CH (65)
980(w)	-	677	651	72.99	1.53	679	653	0.00	0.04	ω CH (64)
850(ms)	852(vw)	677	651	10.67	0.33	673	647	68.34	0.09	ω CH (66)

812(ms)	-	641	616	17.18	21.98	640	615	78.99	24.20	vCCl(75)
800(s)	800(vw)	552	531	0.00	0.24	545	524	0.00	0.17	vCCl(76)
784(s)	-	519	499	21.10	0.12	515	495	65.08	0.17	bCO(72)
680(vs)	-	458	440	0.00	0.22	460	442	16.04	0.09	bCO(73)
-	632(w)	447	430	25.27	104.06	443	426	0.00	97.26	tR1 symd (68)
620(s)	-	412	396	0.66	55.48	420	404	26.90	0.06	bCCl(73)
480(s)	480(ms)	411	395	1.82	0.05	408	392	0.00	74.34	bCCl(72)
-	410(vw)	362	348	0.00	2.54	361	347	25.07	2.70	tR1 trigd (69)
-	392(vw)	347	334	0.23	7.31	344	331	1.87	8.26	tR1 asymd (68)
-	350(w)	323	310	0.38	1.06	324	311	0.15	0.98	tR2 symd (65)
-	284(w)	298	286	3.79	0.28	298	286	0.00	0.46	tR2 trigd (64)
-	228(vw)	226	217	3.07	0.16	227	218	0.26	0.13	tR2 asymd (66)
-	214(ms)	224	215	0.00	1.75	224	215	0.39	1.87	ω CO (64)
-	190(w)	218	210	0.13	1.31	222	213	4.61	1.42	ω CO (63)
-	154(vw)	153	147	0.00	0.03	157	151	3.19	0.02	ω CCl (65)
-	-	74	71	4.76	1.57	81	78	0.00	1.51	ω CCl (63)
-	-	63	61	0.00	0.97	74	71	0.09	0.99	Butterfly(59)

Abbreviations used: v-stretching; β-in-plane bending; γ-out-of-plane bending; R_{sym}-ring symmetric; R_{asym}-ring asymmetric; R_{trig}-ring trigonal; τ-torsion; s-strong; vs-very strong; ms-medium strong; w-weak; vw-very weak.

Table-3: Thermodynamic Properties for 2,3-Dichloro-1,4-Naphthoquinone

Parameters	Method/Basis set	
	B3LYP/6-31+G(d,p)	B3LYP/6-311++G(d,p)
Optimized global minimum Energy (Hartrees)	-1454.23632159	-1454.40258930
Total energy(thermal), E _{total} (kcal mol ⁻¹)	76.939	76.418
Heat capacity, C _v (kcal mol ⁻¹ K ⁻¹)	0.042939	0.043052
Entropy, S (kcal mol ⁻¹ K ⁻¹)		
<i>Total</i>	0.103059	0.102526
<i>Translational</i>	0.042148	0.042148
<i>Rotational</i>	0.030876	0.030876
<i>Vibrational</i>	0.030034	0.029501
Vibrational energy, E _{vib} (kcal mol ⁻¹)	75.162	74.640
Zero point vibrational energy, (kcal mol ⁻¹)	70.01215	69.50891
Rotational constants (GHz)		
<i>A</i>	0.87707	0.87707
<i>B</i>	0.45778	0.45778
<i>C</i>	0.30079	0.30079
Dipole moment (Debye)		
μ _x	0.0000	0.0000
μ _y	0.0000	0.0000
μ _z	3.9308	3.8577
μ _{total}	3.9308	3.8577

UV-Vis and HOMO-LUMO Analysis

The frontier molecular orbitals (FMOs) play an important role in the electric and optical properties, as well as in UV-vis spectra and chemical reactions²³. The energetic behavior of the title compound was evaluated by carrying out calculations in methanol, diethyl ether, benzene and gas phase by using TD-DFT/B3LYP/6-311++G(d,p) method. The calculated absorption wavelengths (λ), oscillator strengths (f) and excitation energies (E) are given Table-4. The theoretical ultraviolet spectrum of DCNQ in gas and solvent phase is shown in Fig-4. According to the Frank-Condon principle, the maximum absorption peak ($\lambda_{\max}$) in a UV-visible spectrum corresponds to vertical excitation. The TD-DFT calculations predict three transitions in the UV-vis region for DCNQ molecule. The strong transitions at 3.0702 eV (403.83 nm) with an oscillator strength $f = 0.003$ in gas phase, at 3.0734 eV (403.41 nm) with an oscillator strength $f = 0.0032$ and at 3.1022 eV (399.66 nm) with an oscillator strength $f = 0.0052$ in methanol and

diethyl ether, respectively, are assigned to a $\pi \rightarrow \pi^*$ transition. For benzene solvent, the strong transitions are found at 3.1201 eV (397.38 nm) with an oscillator strength $f = 0.0081$. The major contributions of the transitions were designated with the aid of SWizard program²⁴. In view of calculated absorption spectra, the maximum absorption wavelength corresponds to the electronic transition from the highest occupied molecular orbital HOMO to lowest unoccupied molecular orbital LUMO with 98 % contribution and is assigned to $\pi \rightarrow \pi^*$ transition. The absorption wavelength corresponds to the electronic transition from HOMO-2 to LUMO (97%) and from HOMO-4 to LUMO (96%) are also assigned to $\pi \rightarrow \pi^*$ type.

Table-4: The Calculated Absorption Wavelength λ (nm), Excitation Energies E (eV) and Oscillator Strengths (f) of DCNQ Calculated by the TD-B3LYP/6-311++G(d,p) Method.

Solvent/Gas Phase	TD-B3LYP/6-311++G(d,p)			Major Contribution	Assignment
	λ (nm)	E (eV)	f		
Methanol	412.77	3.0037	0.0000	H-2 $\rightarrow$ L (97%)	$\pi \rightarrow \pi^*$
Diethyl ether	417.05	2.9729	0.0000		
Benzene	420.12	2.9512	0.0000		
Gas	412.30	3.0071	0.0000		
Methanol	403.41	3.0734	0.0032	H $\rightarrow$ L (98%)	$\pi \rightarrow \pi^*$
Diethyl ether	399.66	3.1022	0.0052		
Benzene	397.38	3.1201	0.0081		
Gas	403.83	3.0702	0.0030		
Methanol	382.81	3.2388	0.0000	H-4 $\rightarrow$ L (96%)	$\pi \rightarrow \pi^*$
Diethyl ether	387.11	3.2028	0.0000		
Benzene	390.20	3.1775	0.0000		
Gas	382.34	3.2428	0.0000		

It is well known that the LUMO represents the ability to obtain an electron and HOMO represents the ability to donate. The electron transfer from ED groups to the efficient EA groups take place through π -conjugated path²⁵. The energies of four important molecular orbitals of DCNQ were calculated using TD-B3LYP/6-311++G(d,p) and are presented in Table 5. The 3D plots of the HOMO-2, HOMO-4, HOMO, and LUMO orbitals computed at the B3LYP/6-311G++(d,p) level for DCNQ (in the gas phase) are illustrated in Fig.-5.

In DCNQ, the HOMO is located over chlorine and oxygen atoms and LUMO: of π nature is delocalized over the whole C-C bond of the fused ring; consequently the HOMO $\rightarrow$ LUMO transition implies an electron density transfer to the C-C bond of the fused ring system from chlorine and oxygen atoms. Moreover, these orbital significantly overlap in their position for DCNQ. The HOMO-LUMO energy gap signifies the eventual charge transfer interaction within the molecule, and the biological activity of the molecule is influenced by this. Furthermore, in going from the gas phase to the solvent phase, there is increasing value of the energy gap and the molecule becomes more stable. The frontier orbital gap in case of DCNQ is found to be 3.82, 3.8393, 3.8513, 3.8178 eV for methanol, diethyl ether, benzene and gas phase, respectively as shown in Table-5. The decrease in energy gap between HOMO and LUMO facilitates intra molecular charge transfer which makes the material to be NLO active.

The total energies and the Koopmans' theorem are used to calculate the electronic properties of the molecule. The ionization potential is determined as $IP = E_{\text{cation}} - E_n = -E_{\text{HOMO}}$ where E_{cation} is the energy of radical cation and E_n is that of the neutral compound. The electron affinity is computed from the energy difference between the neutral molecule and the anion molecule: $EA = E_n - E_{\text{anion}} = -E_{\text{LUMO}}$. The other important quantities such as electronegativity (χ), hardness (η), softness (ξ), and electrophilicity index (ψ) were deduced from ionization potential and electron affinity values²⁶.

$$\begin{aligned} \text{Electronegativity } (\chi) \mu &\approx -\chi = \frac{IP + EA}{2} \\ \text{Hardness } (\eta) &\approx \frac{IP - EA}{2} \\ \text{Softness } (\xi) &\approx \frac{1}{\eta} \end{aligned}$$

$$\text{Electrophilicity index } (\psi) \approx \frac{\mu^2}{2\eta}$$

Fig.-4: Theoretically Calculated UV Spectra in Gas and Solvent Phase for 2,3-Dichloro-1,4-Naphthoquinone.

The values of electro negativity, chemical hardness, softness, and electrophilicity index of DCNQ are 5.7474, 1.91, 0.5235 and 8.6472 eV in methanol, respectively. The most stable structure should have maximum hardness value which being a minimum energy structure at constant chemical potential and hence the principle of maximum hardness has been proved in the present study.

Table-5: Calculated HOMO-LUMO Energy Values of 2,3-Dichloro-1,4-Naphthoquinone Calculated in Gas and Solvent Phase

Parameters	TD-B3LYP/6-311++G(d,p)			
	Methanol	Diethyl ether	Benzene	Gas
E _{HOMO} energy (eV)	-7.6574	-7.6849	-7.7004	-7.6539
E _{LUMO} energy (eV)	-3.8374	-3.8456	-3.8491	-3.8361
ΔE _{HOMO-LUMO energy gap} (eV)	3.82	3.8393	3.8513	3.8178
Electronegativity χ (eV)	5.7474	5.7652	5.7747	5.745
Chemical hardness η (eV)	1.91	1.9196	1.9256	1.9089
Softness ξ (eV) ⁻¹	0.5235	0.5209	0.5193	0.5238
Electrophilicity index ψ (eV)	8.6472	8.6574	8.6589	8.6450
Dipole moment (Debye)	4.5947	4.2754	4.0171	4.6260

NBO Analysis

The interpretation of quantum chemical results, in terms of chemically significant terms, can be done using Natural Bond Orbital (NBO) analysis as one of the most powerful tools. This method localizes the molecular wave functions in optimized electron pairs, corresponding to lone pairs; core pairs on bonding units; giving a picture which is close to the familiar Lewis picture of molecular structure. In the present study, the NBO calculations were performed on DCNQ using NBO 3.1 program as implemented in the Gaussian 09 package at the DFT/B3LYP level. This helps to know the different molecular interactions between the filled and vacant orbitals, which is the measure of the delocalization. An insight into the most important delocalization schemes was obtained by the use of the second-order bond–antibond (donor–acceptor) NBO energetic analysis. The change in electron density (ED) of (σ*, π*) antibonding orbitals and E(2) energies have been calculated by NBO analysis using DFT method to give clear evidence of stabilization originating from various molecular interactions. The hyperconjugative interaction energy was deduced from the second-order perturbation approach²⁷. The stabilization energy E₂ associated with the delocalization $i \rightarrow j$, for each donor (i) and acceptor (j), is estimated as:

$$E_2 = \Delta E_{ij} = q_i \frac{F(i, j)^2}{\epsilon_i - \epsilon_j}$$

Where, q_i is the donor orbital occupancy, ϵ_i and ϵ_j are diagonal elements and $F(i, j)$ is the off-diagonal NBO Fock matrix element. The intramolecular charge transfer is one of the strongest causes of NLO activity. The second order perturbation theory analysis of Fock matrix in NBO basis of DCNQ (Table 6) indicates the intramolecular interactions due to the orbital overlap of $\pi(C_1-O_{11})$ with $\pi^*(C_2-C_3)$, resulting in high electron density (approx. 0.198e) of anti-bonding π orbitals (C-C) which causing stabilization of 12.22 kcal/mol to the system. Similarly, the charge transfer from $\pi(C_5-C_6)$ to $\pi^*(C_7-C_8)$ amounts to the stabilization of 18.32 kcal/mol and the charge transfer from $\pi(C_9-C_{10})$ to $\pi^*(C_7-C_8)$ amounts to the stabilization of 17.21 kcal/mol. Further, the magnitude of charge transfer from the lone pairs of O11 to anti-bonding C1–C2, σ orbital amount to the stabilization of 8.04 kcal/mol, while the lone pairs of chlorine $n3(Cl_{12}) \rightarrow \pi^*(C_2 - C_3)$ and oxygen $n2(O_{14}) \rightarrow \sigma^*(C_3 - C_4)$, it is of the order of 16.66 and 8.27 kcal/mol, respectively. These interactions are responsible for a pronounced decrease of the lone pair orbital occupancy than the other occupancy, and there is a possibility for hyperconjugation between chlorine, oxygen atoms and the aromatic ring.

Mulliken Atomic Charges

In the application of quantum mechanical calculations to molecular systems, the calculation of effective atomic charge plays an important role²⁸. The electron population of each atom as defined by the basis function was determined and the Mulliken atomic charges are calculated at B3LYP method, using 6-31+G(d, p) and 6-311++G(d, p) basis sets, and are combined in Table-7. The calculated charges by B3LYP/6-31+G(d, p) are relatively lesser than 6-311++G(d, p) basis set. The results show that the substitution of the aromatic ring by chlorine and oxygen atoms leads to a redistribution of electron density. The carbon atoms C1 and C4 have the negative (-2.498) charge when compared with all other

ring carbon atoms as shown in the histogram (Fig.-6). This is due to the attachment of oxygen atoms in the ring and all the hydrogen atoms have a net positive charge. In particular, the hydrogen atom both H15 and H18 have charge of 0.214 by B3LYP/6-311++G(d, p) method owing to bound with more electronegative oxygen atoms. The negative values on C5, C6, C7 and C8 atom in the aromatic ring lead to a redistribution of electron density. Due to this strong negative charges, C2 and C3 accommodate higher positive charge, since they are attached with chlorine atoms.

Fig.-5: The Atomic Orbital Compositions of the Frontier Molecular Orbital for 2,3-Dichloro-1,4-Naphthoquinone.
Table-6: Second-order Perturbation Theory Analysis of Fock Matrix in NBO Basis for DCNQ

Donor (i)	ED (i) (e)	Acceptor (j)	ED (j) (e)	^a E(2) (kJ mol ⁻¹)	^b E(j)-E(i) (a.u.)	^c F (i,j) (a.u.)
σ (C1 - C2)	1.97755	σ^* (C3 - Cl13)	0.02904	3.99	0.89	0.053
σ (C1 - C9)	1.96989	σ^* (C2 - Cl12)	0.02901	4.36	0.85	0.054
π (C1 - O11)	1.98831	π^* (C2 - C3)	0.30183	12.22	0.29	0.055
σ (C2 - C3)	1.98018	σ^* (C4 - O14)	0.01793	3.00	1.06	0.051
π (C2 - C3)	1.75084	π^* (C1 - O11)	0.30654	27.02	0.26	0.076
		π^* (C4 - O14)	0.30654	27.11	0.26	0.076
σ (C3 - C4)	1.97677	σ^* (C2 - Cl12)	0.02901	3.99	0.89	0.053
σ (C4 - C10)	1.96927	σ^* (C3 - Cl13)	0.02904	4.37	0.85	0.055
		σ^* (C5 - C10)	0.04018	4.03	1.26	0.064
π (C4 - O14)	1.98735	π^* (C2 - C3)	0.30183	12.23	0.29	0.056
π (C5 - C6)	1.97946	π^* (C7 - C8)	0.26839	18.32	0.28	0.067
σ (C7 - C8)	1.98085	σ^* (C6 - H16)	0.01268	4.04	1.18	0.062
		σ^* (C9 - C10)	0.03570	32.95	5.77	0.391
		π^* (C9 - C10)	0.46619	3.94	2.96	0.109
π (C7 - C8)	1.59472	π^* (C5 - C6)	0.26839	17.62	0.28	0.065
σ (C7 - H17)	1.98149	σ^* (C5 - C6)	0.01424	3.49	1.08	0.055
		σ^* (C8 - C9)	0.02335	3.57	1.08	0.056
σ (C8 - C9)	1.97124	σ^* (C1 - C9)	0.03982	4.07	1.22	0.063
		σ^* (C9 - C10)	0.03570	65.39	5.74	0.548
		π^* (C9 - C10)	0.46619	7.49	2.94	0.150
σ (C8 - H18)	1.97951	σ^* (C7 - H17)	0.01254	4.42	0.99	0.059
		σ^* (C9 - C10)	0.03570	107.48	5.57	0.693
σ (C9 - C10)	1.96091	σ^* (C5 - C10)	0.02395	4.31	1.24	0.066
		σ^* (C8 - C9)	0.02335	4.50	1.26	0.067
π (C9 - C10)	1.58895	π^* (C1 - O11)	0.30654	32.25	0.22	0.077
		π^* (C4 - O14)	0.30654	32.36	0.22	0.077
		π^* (C5 - C6)	0.26839	17.05	0.29	0.065
		π^* (C7 - C8)	0.26839	17.21	0.29	0.066
n2(O ₁₁)	1.94950	σ^* (C1 - C2)	0.04500	8.04	0.78	0.071
		σ^* (C1 - C9)	0.03982	7.22	0.79	0.068
n2(Cl ₁₂)	1.96669	σ^* (C1 - C2)	0.04500	4.72	0.83	0.056
		σ^* (C2 - C3)	0.03962	4.05	0.83	0.052
n3(Cl ₁₂)	1.88042	π^* (C2 - C3)	0.30183	16.66	0.29	0.065
n2(Cl ₁₃)	1.96666	σ^* (C2 - C3)	0.03962	4.06	0.83	0.052
n3(Cl ₁₃)	1.88042	π^* (C2 - C3)	0.30183	16.66	0.29	0.065
n2(O ₁₄)	1.94958	σ^* (C3 - C4)	0.04566	8.27	0.76	0.071
		σ^* (C4 - C10)	0.04018	7.25	0.77	0.067
π^* (C1 - O11)	0.30654	π^* (C2 - C3)	0.30183	109.03	0.02	0.083
π^* (C4 - O14)	0.30654	π^* (C2 - C3)	0.30183	105.31	0.02	0.083

^aE(2) means energy of hyperconjugative interactions.^bEnergy difference between donor and acceptor i and j NBO orbitals.^cF(i,j) is the Fock matrix element between i and j NBO orbitals.

Table-7: The Mulliken Charge Distribution of 2,3-Dichloro-1,4-Naphthoquinone

Atoms	Atomic Charges (Mulliken)	
	B3LYP/6-31+G(d,p)	B3LYP/6-311++G(d,p)
C1	-1.255613	-2.498711
C2	0.513028	1.344374
C3	0.513028	1.344374
C4	-1.255613	-2.498711
C5	-0.014917	-0.053375

C6	-0.143521	-0.378171
C7	-0.143521	-0.378171
C8	-0.014917	-0.053375
C9	0.614283	0.863209
C10	0.614283	0.863209
O11	-0.402030	-0.228303
Cl12	0.332209	0.547916
Cl13	0.332209	0.547916
O14	-0.402030	-0.228303
H15	0.180834	0.214531
H16	0.145892	0.188531
H17	0.145892	0.188531
H18	0.180834	0.214531

Electrostatic Potential, Total Electron Density and Molecular Electrostatic Potential

For predicting sites and relative reactivities towards electrophilic attack, and in studies of biological recognition and hydrogen bonding interactions, the electrostatic potential has been utilized²⁹. The MEP at the B3LYP/6-311++G(d,p) optimized geometry is calculated, and reactive sites for the electrophilic and nucleophilic attack are predicted for the investigated molecule.

Fig.-6: Mulliken's Plot for 2,3-Dichloro-1,4-Naphthoquinone.

In the present investigation, the electrostatic potential (ESP), electron density (ED) and the molecular electrostatic potential (MEP) map figures for DCNQ are shown in Fig.-7. The ED plots for DCNQ show a uniform distribution. However, it can be seen from the ESP figures, that the negative ESP is localized more over the oxygen atoms and is reflected as a yellowish blob, the positive ESP is localized on the rest of the molecule.

Fig.-7: (a) Electrostatic Potential (ESP); (b) Electron Density (ED) and (c) the Molecular Electrostatic Potential (MEP) map for 2,3-Dichloro-1,4-Naphthoquinone.

This result is expected, because ESP correlates with electro negativity and partial charges. The negative (red and yellow) regions of the MEP are related to electrophilic reactivity and the positive (blue) regions to nucleophilic reactivity, as shown in Fig.-7. Generally, the potential energy increases from red < orange < yellow < green < blue. In the present study, the MEP map shows that the negative potential sites are on oxygen atoms (Red) and the positive potential sites are around the hydrogen atoms of the ring (Blue).

From these results, one can say that the H atoms indicate the strongest attraction and oxygen atoms indicate the strongest repulsion. The information about the region of intermolecular interactions for the title compound is provided by these sites. Thus, the results indicate that the DCNQ will be the most reactive site for both electrophilic and nucleophilic attack.

CONCLUSION

Based on the scaled quantum mechanical force field obtained by DFT/B3LYP method with 6-31+G(d,p) and 6-311++G(d,p) basis sets, complete vibrational properties of 2,3-dichloro-1,4-naphthoquinone have been investigated by FTIR and FT-Raman spectroscopies. Based on the results of the TED output, the assignments of various modes of vibrations were carried out unambiguously. The ability of the methodology applied for interpretation of the vibrational spectra was confirmed by these results. The eventual charge transfer interactions taking place within the molecule was explained by the HOMO and LUMO energy gap. The charge transfer, mainly due to the lone pair $n3(Cl_{12}) \rightarrow \pi^*(C_2 - C_3)$ and $n2(O_{14}) \rightarrow \sigma^*(C_3 - C_4)$, is reflected in the NBO results. The UV spectra of the title compound were calculated to evaluate the electronic transitions and charge distribution. From the theoretical molecular orbital coefficient analysis, it can be inferred that electronic transitions are assigned to $\pi \rightarrow \pi^*$ type. Furthermore, the first hyperpolarizability, Mulliken's charge, molecular electrostatic potential and thermodynamic properties of the title molecule have been calculated and the results are discussed. These results indicate that the DCNQ compound is a good candidate of nonlinear optical materials.

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