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Spectroscopic characterization and DFT exploration of 2-(4-methoxybenzyloxy)-4-methylquinoline

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ABSTRACT

In this study, the FT-IR and FT-Raman spectra of 2-(4-methoxybenzyloxy)-4-methylquinoline(MBMQ) have been recorded in the regions 4000–400cm^{-1} and 3500–50cm^{-1} respectively. The molecular structure and fundamental vibrational frequencies have been obtained from density functional theory (DFT) B3LYP method with 6-311++G(d,p) basis set calculations. Global reactivity descriptors such as electronegativity(χ), hardness(η), softness(S), chemical potential(μ) and electrophilicity index(ω) have been calculated from HOMO and LUMO energies. Molecular electrostatic potential (MEP) of the title compound was calculated to predict reactive behaviour of the molecule. The local reactivity has been analysed through the Fukui functions in order to predict the possible sites of nucleophilic and electrophilic attacks. The thermodynamic properties at different temperatures were calculated, revealing the correlations between standard heat capacities, standard entropy and standard enthalpy changes with temperatures.

Keywords: spectroscopic, 2-(4-methoxybenzyloxy)-4-methylquinoline, DFT, MEP and Fukui function.

INTRODUCTION

Quinoline and its derivatives have been extensively explored for their chemical and biological properties. They possess pharmacological activities including antimalarial[1], antitumour[2], antibacterial [3] and anti-arteriostenotic and useful in the treatment of tuberculosis, diabetes, and convulsion [4,5].Some quinoline derivatives has been reported as effective corrosion inhibitors for mild steel in acidic medium [6]. In this work the solid phase experimentally observed spectral data (FT-TR and FT-Raman) of the title compound is compared with the gas phase theoretical calculation data obtained by DFT/B3LYP method. The molecular properties like global reactivity descriptors, molecular electrostatic potential surface, thermodynamic parameters, have been calculated to get a better insight of the properties of the title molecule. Local reactivity descriptors like Fukui functions, local softness have been computed to predict reactivity and reactive sites on the molecule.

MATERIALS AND METHODS

Experimental details

The compound under investigation MBMQ was procured from Sigma–Aldrich chemicals, U.S.A with a stated purity of greater than 98%. The compound was used as such without further purification. The FT-IR spectrum of the compound was recorded in the region 4000-400cm^{-1}on a Perkin Elmer FT-IR Spectrophotometer. The FT-Raman spectrum of the title compound was recorded in the Bruker FRA 106/S instrument equipped with Nd:YAG laser source operating at 1064 nm line widths in the range of 3500–50cm^{-1}. The spectral measurements were carried out at Sophisticated Analytical Instrument Facility, IIT, Chennai, India.

Computational details

The gas phase geometry of the compound under investigation MBMQ in the ground state was optimized by using DFT/B3LYP level with the standard basis set 6-311++G(d,p) using Gaussian 09W [7] program package, invoking gradient geometry optimization [8]. The scaling factors have to be used to obtain considerably better agreement with experimental data. The computed harmonic frequencies at B3LYP/6-311++G(d,p) level of basis set were scaled by 0.981 for frequencies less than 1700cm^{-1} and 0.9615 for higher frequencies[9]. From the value of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO),the global reactivity descriptors like global hardness (η) ,global softness (S), electronegativity(χ) and chemical potential (μ) have been calculated. The local reactivity has been analyzed by means of the Fukui indices, since they indicate the reactive regions, in the form of the nucleophilic and electrophilic behaviour of each atom in the molecule. To visualize variably charged regions of a molecule in terms of colour grading the molecular electrostatic potential (MEP) map have been plotted. On the basis of theoretical frequencies obtained from density functional calculations at B3LYP/6-311++G(d,p) level, the statistical standard thermodynamic parameters likeentropy (S), Heatcapacity (C) and enthalpy (H) were calculated.

RESULTS AND DISCUSSION

Molecular geometry

The title molecule consists of two rings. One quinoline and other benzyloxy ring. The optimized molecular structure along with the numbering of atoms of 2-(4-methoxybenzyloxy)-4-methylquinoline (MBMQ),obtained from GaussView program is shown in Fig.1. The global minimum energy obtained by the DFT/ B3LYP/6-311++G(d,p) for the optimized structure of the title compound is -901.5965Hartrees.

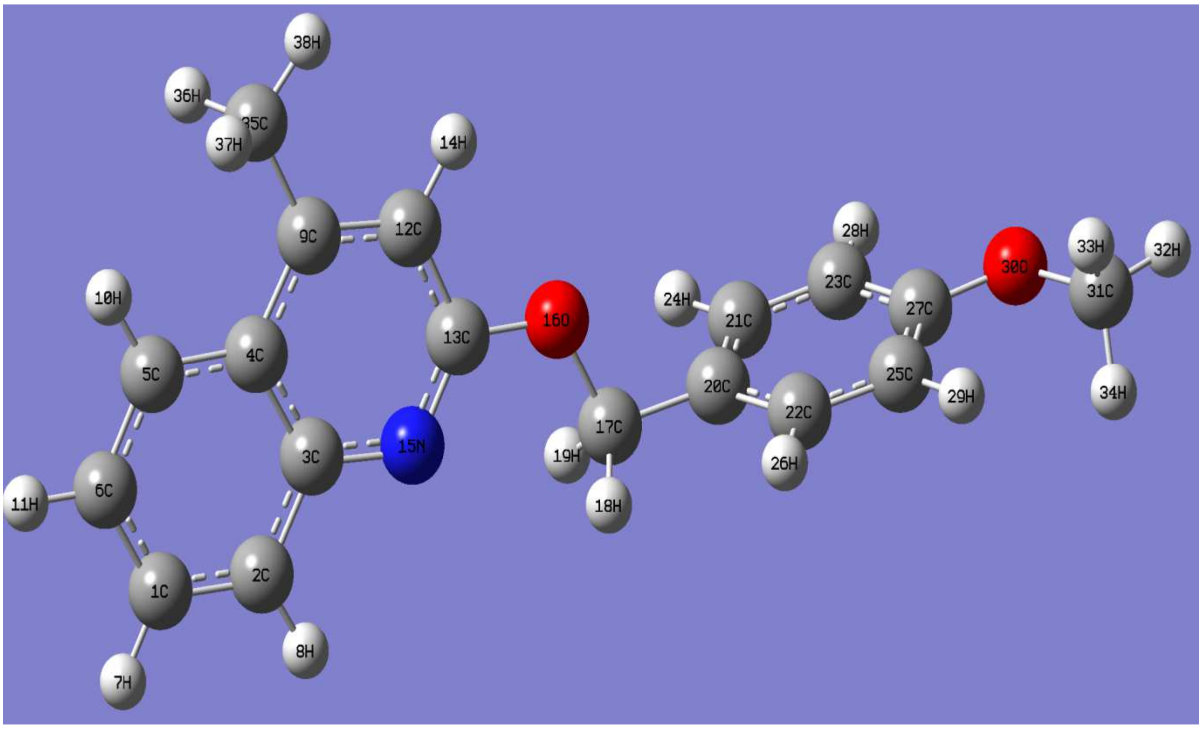


Fig.1 Optimized structure and atoms numbering of 2-(4-methoxybenzyloxy)-4-methylquinoline (MBMQ)

Vibrational spectral analysis

The objective of the vibrational analysis is to find the vibrational modes connected with the molecular structure of the title compound. The geometry of the title molecule is considered as C1 point group symmetry. The studied molecule consists of 38 atoms having 108 modes of vibration and most of the modes are active in both IR and Raman spectra. The selected vibrational assignments of fundamental modes of MBMQ along with observed and calculated frequencies are reported in Table 1. The calculated and experimental FT-IR, FT-Raman spectra are shown in Figs. 2 and 3 respectively.

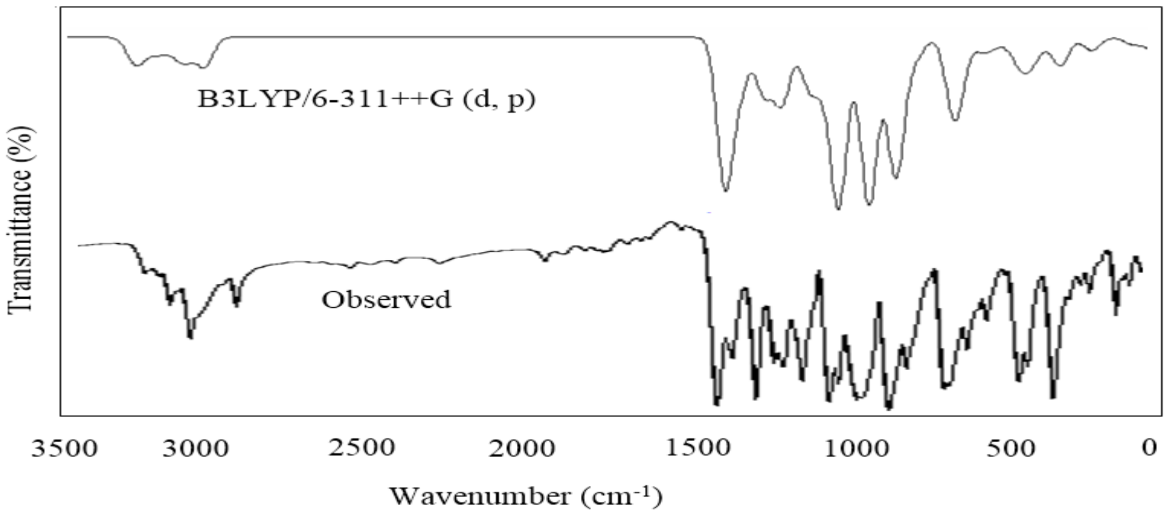


Fig. 2 Observed and calculated FT-IR spectra of 2-(4-methoxybenzyloxy)-4-methylquinoline (MBMQ)

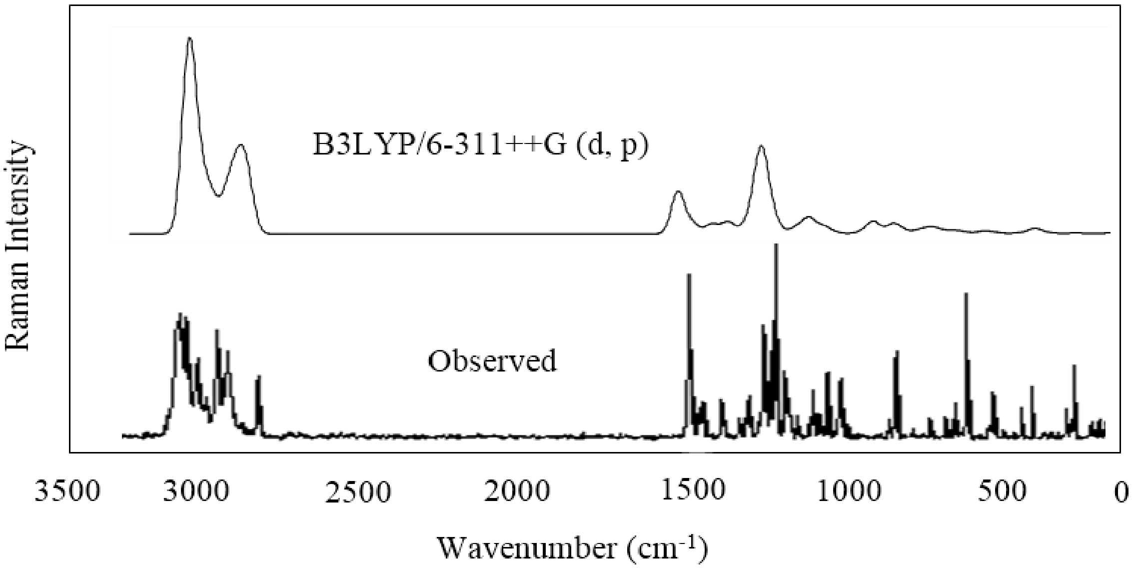


Fig. 3Observed and calculated FT-Raman spectra of 2-(4-methoxybenzyloxy)-4-methylquinoline (MBMQ)

C-C vibrations

Carbon stretching vibrations are very much prominent in the spectrum of benzene and its derivatives. The C–C stretching vibrations are normally found at 1400 – 1650cm^{-1} in benzene derivatives [10,11].In general, the bands are of variable intensity and are observed at 1625–1590, 1590–1575, 1540–1470,1465–1430 and 1380–1280cm^{-1} from the wavenumber ranges given by Varsanyi [12] for the five bands in this region. In the present work, the wavenumbers observed at 1612, 1573 in the FT-IR spectrum and the same observed at 1632, 1612 1589 and 1584cm^{-1} in FT-Raman spectra have been assigned to C- C stretching vibrations. The theoretically computed values at 1619, 1626,1590 and 1578cm^{-1}show an excellent agreement with the observed experimental data.

The very strong band observed at 664cm^{-1} in the FT-IR spectrum and 665cm^{-1} in FT-Raman spectrum of MBMQ has been assigned to the ring-breathing vibration. The computed wavenumber at 677cm^{-1} by the B3LYP/6-311++G(d,p) method coincide well with the experimental observation. The band observed at 843cm^{-1} in FT-IR and 848,1010cm^{-1} in FT-Raman spectra has been assigned to C-C-C deformation vibrations of the title compound. The theoretically computed value at 852,1010cm^{-1} is well correlated with the experimental observations.

C-H vibrations

Aromatic compounds commonly exhibit multiple weak band in the region 3100–3000cm^{-1} due to aromatic C–H stretching vibrations [13]. In the present study, the bands appeared at 3007,3034,3045 and 3070cm^{-1} in FT-IR and 3001,3043,3062 and 3070cm^{-1} in FT-Raman spectra are assigned to C-H stretching vibrations both in quinoline and benzyloxy ring. This experimental bands are well agreed with the theoretically calculated wavenumbers at 3002,3030,3042,3060 and 3070cm^{-1}by B3LYP method. The C–H in-plane bending vibrations generally occurs in the region 1300–1000cm^{-1}[14]. In accordance with the data obtained from the literature, the bands observed at 1130,1175,1180cm^{-1}in FT-IR and 1134,1179 and 1196cm^{-1} in FT-Raman spectra are assigned to C-H in-plane bending mode of vibrations. The calculated wavenumbers at 1133,1175 and 1187cm^{-1} are well correlated with the experimental values. The C-H out-of plane bending vibrations normally occur in the region 1000-700cm^{-1} [15]. They are not very much affected by the nature of substitution. In the present study, the bands observed at 768,821,926,948 and 975cm^{-1} inFT-IR and 773,822,926,945 and 975cm^{-1} in FT-Raman spectra are assigned to C-H-out of plane bending vibrations. The theoretically calculated wavenumbers at 779,827,925,948 and 974 cm^{-1} are well agreed with the experimental observations.

O-CH$_3$ group vibrations

In the present study, the molecule MBMQ has one methoxy group attached with the benzyloxy ring. Generally the C-H stretching vibrations in methoxy group has been observed at lower wavenumber than the normal C-H stretching wavenumber for methyl group [16]. In aromatic methoxy compounds, asymmetric vibration of CH$_3$ found in the region of 2985 ± 20cm^{-1}[17]. The calculated value at 2982 cm^{-1}by B3LYPmethod is confirmed by the presence of a strong band at 2985cm^{-1} in FT-IR and 2975cm^{-1} in FT-Raman for this mode. The same is observed in the CH$_3$ group attached with the quinoline ring at 3007cm^{-1} in FT-IR and 3001cm^{-1} in FT-Raman spectra. This is well correlated with the theoretically calculated wavenumber at 3002cm^{-1}.The calculated wavenumber at 2878cm^{-1} is well correlated with the experimentally observed bands at 2872 cm^{-1} both in FT-IR and FT-Raman spectra which is assigned to CH$_3$ symmetric stretching mode of vibration. In the case of CH$_3$ group attached with the quinoline ring, the symmetric stretching mode of vibration observed at 2889cm^{-1} in FT-Raman spectra is well aligned with the theoretically calculated value at 2900cm^{-1}. The asymmetric and symmetric stretching vibration of C-O-C in methoxy group attached to an aromatic ring appeared in the range of 1310–1210cm^{-1} and 1050–1010cm^{-1}[18]. The theoretically calculated value at 1253cm^{-1}and 1043cm^{-1}is supported by the strong bands observed at 1257cm^{-1}in FT-IR and 1259 and 1047cm-^{1} in FT-Raman spectra which is assigned to C-O-C asymmetric and symmetric stretching mode of vibrations. The O-CH$_3$ in plane bending mode has been calculated by B3LYPmethodat 581cm^{-1}. This is confirmed by the presence of a strong band at 596cm^{-1}FT-IR and 583 cm^{-1} in FT-Raman spectra as well as the literature value [19]. CH3 torsional mode is identified at 155, 165cm^{-1}by calculated values is confirmed by the presence of a Raman band at 150,161cm^{-1}. O-CH3 torsional mode is calculated by B3LYPmethodat 230cm^{-1}is confirmed by the presence of a strong peak at 234, cm^{-1} in FT-Raman spectra.

C-N Vibrations

The identification of C-N vibration is difficult task, since the mixing of several bands are possible in this region. The C-N stretching vibration usually lies in the region 1200 to 1400 cm^{-1} [20]. In the present work, the frequency observed as very strong band at 1327cm^{-1} in FT-IR and 1317cm^{-1} in FT-Raman spectra have been assigned to C-N stretching vibration. The theoretically computed value at 1327cm^{-1}is well correlated with the experimental observations. The literature value also support this observation [21]. The band observed at 879, 533cm^{-1} in FT-IR and 881, 531cm^{-1}in FT-Raman spectra are assigned to C-N in-plane bending and out-of-plane bending mode vibration. The calculated values at 882, 534cm^{-1} is well agreed with the experimental wavenumbers. These vibrations are almost mixed up with the C-C stretching vibrations.

Molecular electrostatic potential(MEP)

The molecular electrostatic potential (MEP) is related to the electron density and a very useful descriptor for determining sites for electrophilic and nucleophilic attack as well as hydrogen-bonding interactions [22].It is related to total charge distribution of the molecule providing the correlations between the molecular properties such as dipole moments, partial charges, chemical reactivity and electronegativity of molecules [23]. The MEP map of the title compound was calculated by B3LYP/6-311++G(d,p) method. The study of MEP leads to the better understanding of complex biological processes involving the charge-dipole, dipole-dipole, and quadrupole -dipole interactions as well as displays molecular size, shape and electrostatic potential value. At any given point r(x, y, z) in the vicinity of a molecule, the molecular electrostatic potential, V(r) is defined in terms of the interaction energy between the electrical charge generated from the molecule electrons and nuclei and a positive test charge (a proton) located at r [24].

Table.1Selected comparison of the experimental wavenumbers, IR intensity (I_{IR}), Raman intensity (I_{Raman})with the theoretically computed wavenumbers of MBMQ

S.No	FT-IR	FT-Raman	B3LYP	I_{IR}	I_{Raman}	Vibrational Analysis
1			15	0.216	4.395	Lattice vibration
2		150	155	1.238	0.708	τ CH_3
3		161	165	1.956	2.359	τ CH_3
4		225	221	1.011	1.335	τ CH_3
5		300	297	0.205	2.742	ρ CH_3
6		234	230	2.572	0.747	τ O-CH_3
7		429	422	4.398	0.873	γ C-C-C
8	440		429	4.252	0.342	υ C-C-C
9	521	523	522	9.436	8.836	ring breathing
10	533	531	534	2.208	0.149	γ C-N
11	596	583	581	9.053	1.726	β O-CH_3
12	640	643	640	0.636	5.912	υ C-C-C
13	664	665	677	29.866	11.886	ring breathing
14	686	685	695	3.192	0.825	γ C-H
15	716	715	719	1.252	1.669	γ C-H
16	757	755	757	61.472	0.568	γ C-H
17	768	772	773	0.528	0.190	γ C-H, γ C-C, γ C-N
18		773	779	11.394	13.496	γ C-H
19	821	822	827	37.025	19.077	γ C-H
20	843	848	852	44.985	18.078	β C-C-C
21	879	881	882	21.531	13.567	β C-N
22	926	926	925	16.696	10.434	γ C-H
23	948	945	948	1.314	0.533	γ C-H
24	975	975	974	0.138	0.170	γ C-H
25		1010	1010	3.975	0.086	γ C-C-C
26	1019	1022	1020	106.158	48.76	υ C-C-C
27	1033	1036	1036	78.724	7.472	υ C-C-C , υ C-CH_3
28		1042	1041	1.033	0.170	δCH_3
29		1047	1043	41.256	3.106	υs C-O-C
30		1116	1116	10.296	0.455	β C-H
31	1130	1134	1133	39.578	3.499	β C-H
32	1175	1179	1175	149.459	20.022	β C-H
33		1184	1181	26.922	6.932	ρ C-CH_3
34	1180	1196	1187	177.637	5.283	β C-H
35		1227	1226	4.586	6.662	t CH_2
36	1257	1259	1253	303.892	25.523	υ_{as} C-O-C
37	1303	1307	1310	30.057	8.212	β C-H
38	1327	1317	1327	254.219	16.486	υ C-N
39		1365	1368	84.512	350.442	υ C-C, ω CH_2
40	1395	1399	1391	8.564	18.958	ω CH_3
41		1415	1402	97.906	60.098	υ C-O, ω CH_2
42		1425	1425	2.889	1.980	t CH_2, υ C-C, β C-H
43	1443	1453	1450	5.642	4.542	ω O-CH_3
44	1468		1467	9.165	15.169	δ O-CH_3
45		1486	1482	3.942	7.101	δCH_2
46	1514	1519	1520	46.073	6.969	υ C-C-C, β C-H
47	1573	1584	1578	103.215	34.373	υ C-C
48		1589	1590	16.824	13.449	υ C-C
49	1612	1612	1619	265.215	20.704	υ C-C
50		1632	1626	45.525	129.538	υ C-C
51	2872	2872	2878	60.594	181.195	υ_s CH_3
52		2889	2900	20.509	230.061	υ_s CH_3
53	2953	2954	2947	11.636	79.967	$\upsilon_{as}CH_3$
54	2985	2975	2982	16.770	61.997	$\upsilon_{as}CH_3$
55	3007	3001	3002	24.417	155.813	υ C-H, $\upsilon_{as}CH_3$
56	3034		3030	11.209	61.145	υ C-H
57	3045	3043	3042	8.173	136.930	υ C-H
58		3062	3060	13.659	318.580	υ C-H
59	3070	3070	3070	8.954	110.785	υ C-H

υ-stretching; υ_s-sym.stretching; υ_{as}-asym. stretching; β - in-plane-bending; γ - out-of-plane bending; ω - wagging; ρ- rocking; t - twisting; τ - torsion; δ - scissoring.

MEP surface diagram shown in Fig.4 is used to visualize variably charged regions of a molecule in terms of colour grading. Areas of red (negative MEP) are characterized by an abundance of electrons or greatest electron density. Areas of blue (positive MEP), are characterized by a relative absence of electrons. The electrostatic potential increases in the order red < orange < yellow < green < blue. The colour code of the maps in the range -3.945 a.u.(deepest red) to 3.945 a.u.(deepest blue) in the title molecule, where the blue colour indicates the strongest attraction and the red colour indicates the strongest repulsion. As can be seen from the MEP map of the title compound the maximum negative regions V(r) are associated with the lone pair oxygen(O_{16}) atom having value of -0.0389222 a.u. The maximum positive regions localized on the H_{28} atom in the ring have the value of +0.0065448 a.u. However, the H atoms at the O-CH_3 group have smaller values than the H atoms in the ring. From this result, we infer that the oxygen atom indicates the strongest repulsion and H atoms indicate the strongest attraction.

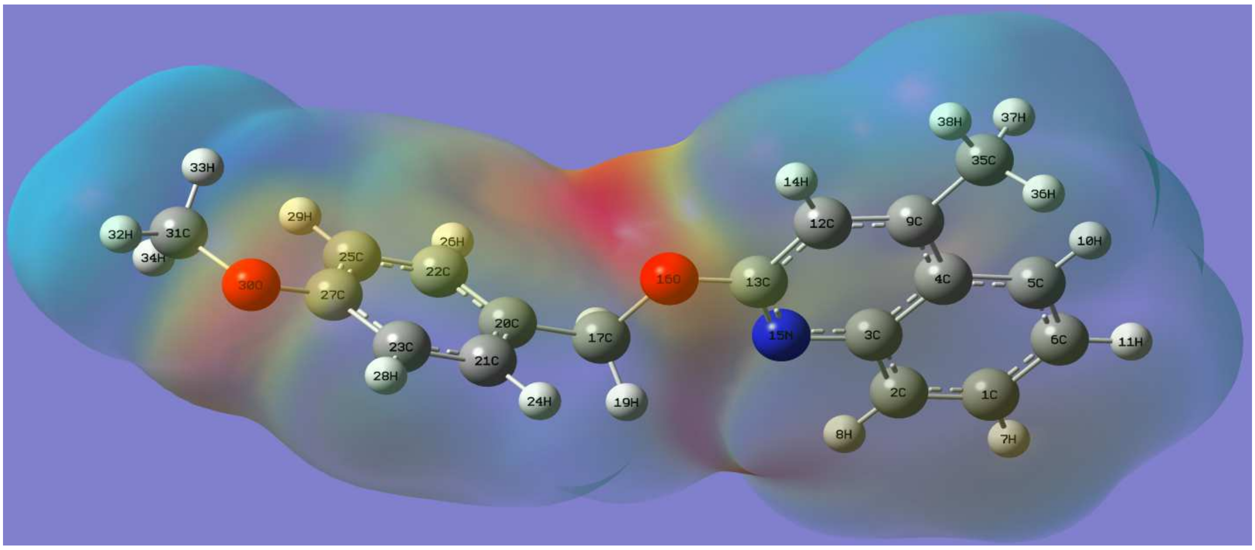
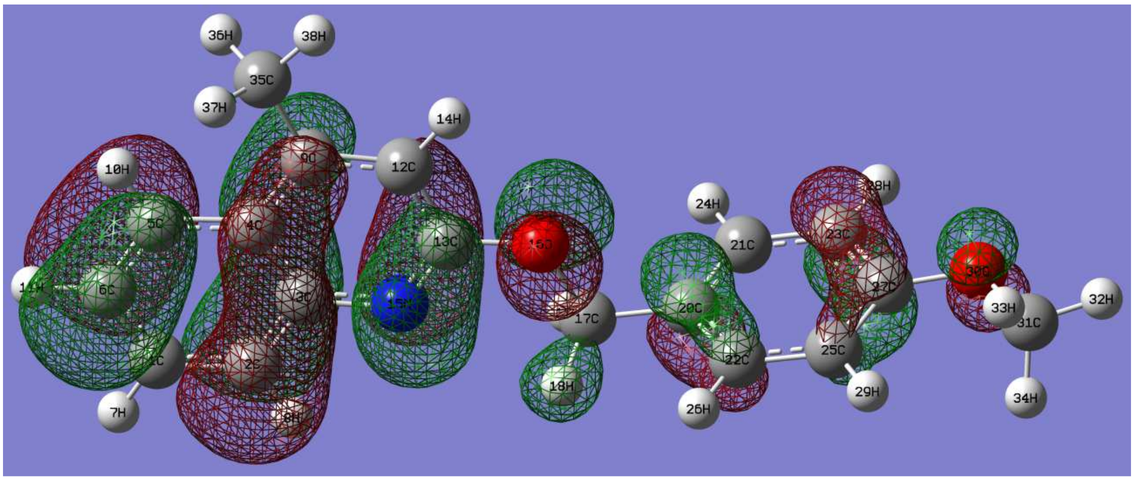


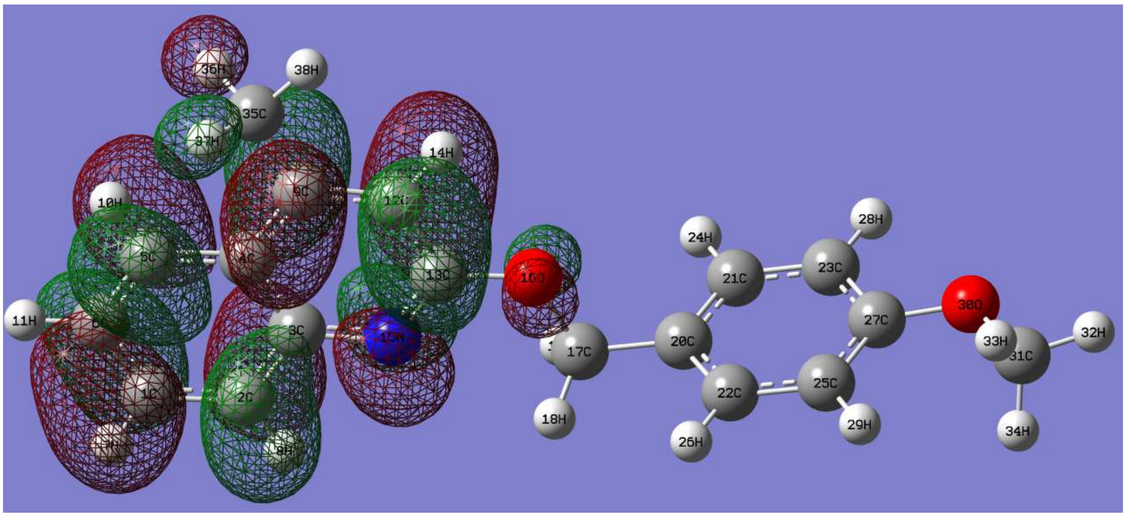
Fig. 4 Molecular electrostatic potential map of 2-(4-methoxybenzyloxy)-4-methylquinoline (MBMQ)

Chemical Reactivity

Conceptual density functional theory (DFT) has been widely used to study the chemical reactivity and site selectivity of various molecular systems[25,26]. The new chemical reactivity descriptors has gained significant role due to their application in various areas of chemistry, biology, computer-aided toxicity prediction and drug design[27].



HOMO of MBMQ



LUMO of MBMQ

Fig. 5 Atomic orbital composition of the frontier molecular orbital for MBMQ

Global reactivity descriptors

Density functional theory has been quite successful in providing theoretical background of popular qualitative chemical concepts and have been used to analyze chemical reactivity and site selectivity. According to the frontier molecular orbital theory (FMO) of chemical reactivity, transition of electron is due to interaction between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of reacting species [28]. The widely used global reactivity descriptors like, global hardness(η), global softness(S) , electronegativity(χ) and chemical potential(μ) and electrophilicity index(ω) are used to understand the global nature of molecules in terms of their stability and also it is possible to gain knowledge about the reactivity of molecules. The calculated global reactivity descriptors Values of MBMQ are tabulated in table 2.

According to, the Koopman's theorem [29] ionization potential (I)and electron affinity (A)can be expressed as follows in terms of E_{HOMO}, E_{LUMO} the highest occupied molecular orbital energy, and the lowest unoccupied molecular orbital energy, respectively

$$I = -E_{HOMO} \qquad (1)$$

$$A = -E_{LUMO} \qquad (2)$$

When the values of *I* and *A* are known, the values of the absolute electronegativity χ, and the absolute hardness η can be determine through the following expressions [30]

$$\chi = I + A/2 \qquad (3)$$

Chemical hardness (η) is obtained from the equation:

$$\eta = I - A/2 \qquad (4)$$

It measures the resistance of an atom to a charge transfer.

Chemical softness(S) describes the capacity of an atom or group of atoms to receive electrons and is the inverse of the global hardness [31]

$$S = \frac{1}{\eta} \qquad (5)$$

Electronegativity, hardness and softness have proved to be very useful quantities in the chemical reactivity theory.

The chemical potential μ, the negative of electronegativity(χ) of a system is useful for describing phase transitions, the stratification of gases in a gravitational field, electric currents in semi-conductor junctions and nuclear reactions [32]. Compounds with negative chemical potential are stable and do not decompose spontaneously into the elements they are composed of.

The absolute electrophilicity index (ω) [33] which is calculated by the equation

$$\omega = \frac{\mu^2}{2\eta} \qquad (6)$$

According to the definition, this index measures the propensity of chemical species to accept electrons. A high value of electrophilicity index describes a good electrophile while a small value of electrophilicity index describes a good nucleophile.

Table 2. HOMO LUMO energy value and related quantum chemical parameters of MBMQ calculated by B3LYP/6-311++G(d,p) method

Parameter	Energy(eV)
E_{HOMO} (eV)	-6.2435
E_{LUMO} (eV)	-1.4501
Energy gap(ΔE)	4.7934
Dipole moment (μ in Debye)	4.5413
Hardness(η)	2.3967
Electronegativity(χ)	3.8468
Softness (*S*)	0.4172
Electrophilicity index(ω)	3.0871
Chemical potential(μ)	-3.8468

Local reactivity descriptors

The local reactivity of the compound under study, was analyzed through an evaluation of the Fukui indices [34]. The condensed Fukui function and local softness indices allow one to distinguish each part of the molecule on the basis of its distinct chemical behaviour [35] due to the different substituted functional group. Their values are used to identify which atoms in the molecule are more prone to undergo an electrophilic or a nucleophilic attack. The regions of a molecule where the Fukui function is large are chemically softer than the regions where the Fukui function is small. The change in electron density is the nucleophilic f^+(r) and electrophilic f^-(r) Fukui functions, can be calculated using the finite difference approximation as follows [36].

$f_k^+ = q_{N+1} - q_N$ for nucleophilic attack (1)

$f_k^- = q_N - q_{N-1}$ for electrophilic attack (2)

where q_N, q_{N+1} and q_{N-1} are the electronic population of the atom k in neutral, anionic and cationic systems.

The local softness s, for an atom can be expressed as the product of the condensed Fukui function(*f*) and the global softness(S) as follows [37]

$s^+ = (f^+) S$ (3)

$s^- = (f^-) S$ (4)

The local softness as like those obtained from the condensed Fukui function also have the additional information about the total molecular softness, which is related to the global reactivity with respect to the reactive agents. A high value of s^+ indicates high nucleophilicity and a high value of s^- high electrophilicity.

Table 3. Fukui and local softness indices for nucleophilic and electrophilic attacks in MBMQatoms calculated from Mulliken atomic charges; Maxima in bold

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
1 C	0.02566	-0.02115	0.01483	-0.01222
2 C	0.05762	-0.08107	0.03330	-0.04685
3 C	0.00853	0.02590	0.00492	0.01497
4 C	-0.03806	0.01866	-0.02199	0.01078
5 C	0.10037	-0.06498	0.05801	-0.03756
6 C	-0.00326	0.16824	-0.00188	0.09724
7 H	0.05104	0.04015	0.02949	0.02321
8 H	0.04846	0.03032	0.02801	0.01752
9 C	-0.05507	0.13628	-0.03183	0.07876
10 H	0.03406	0.03286	0.01968	0.01899
11 H	0.05096	0.04796	0.02945	0.02772
12 C	0.12358	-0.16595	0.07142	-0.09591
13 C	-0.03076	-0.26471	-0.01781	-0.15298
14 H	0.04062	0.03599	0.02342	0.02080
15 N	0.05662	0.14744	0.03272	0.08521
16 O	0.04866	0.08833	0.02812	0.05105
17 C	-0.15945	-0.13507	-0.09215	-0.07801
18 H	0.00905	0.03882	0.00523	0.02244
19 H	0.00693	0.03095	0.00401	0.01788
20 C	-0.13376	**0.91296**	-0.07730	**0.52764**
21 C	-0.12679	-0.44856	-0.07328	-0.25925
22 C	-0.11220	0.24801	-0.06485	0.14333
23 C	-0.02023	-0.01199	-0.01169	-0.00693
24 H	-0.00625	0.03668	-0.00361	0.02120
25 C	0.05843	-0.15443	0.03376	-0.08925
26 H	0.07253	-0.01281	0.04191	-0.00745
27 C	0.28906	-0.14257	0.16706	-0.08241
28 H	0.02156	0.05045	0.01246	0.02915
29 H	0.11252	0.06592	0.06503	0.03810
30 O	0.03835	0.07005	0.02216	0.04048
31 C	-0.68116	0.00030	-0.39367	0.00017
32 H	**0.46884**	0.03528	**0.27096**	0.02039
33 H	0.22064	0.02872	0.12752	0.01660
34 H	0.22233	0.02908	0.12849	0.01681
35 C	0.08024	0.11794	0.04637	0.06816
36 H	0.04696	0.02718	0.02714	0.01571
37 H	0.04718	0.02401	0.02727	0.01387
38 H	0.02616	0.01484	0.01512	0.00857

Thermodynamic properties

On the basis of theoretical frequencies obtained from density functional theory calculations at B3LYP/6-311++G(d,p) level, the statistical standard thermodynamic functions such as heat capacity, entropy and enthalpy were calculated using Perl script THERMO.PL [38] for the title compound and listed in Table 4. It is observed that the standard heat capacities, entropies and enthalpy changes are increasing with temperatures ranging from 100 to 1000 K due to the fact that the molecular vibrational intensities are increasing with temperatures [39].The correlation equations between entropies, heat capacities, enthalpy changes and temperatures were fitted by quadratic formula, and the corresponding fitting factors (R^2) for these thermodynamic properties are 1.0000, 0.9988 and 0.9999, respectively. The corresponding fitting equations are as follows and the correlation graphics of those shows in Fig. 6 and the corresponding fitting equations are given as follows:

$$S = 269.85934+1.16362T-2.10 \times 10^{-4} T^2 \qquad R^2 = 1.0000$$

$$C = 10.72279+1.11411T - 3.90 \times 10^{-4} T^2 \qquad R^2 = 0.9988$$

$$H = -2.33354+0.05490T + 4.10 \times 10^{-4} T^2 \qquad R^2 = 0.9999$$

All the thermodynamic data provide helpful information for further study on the MBMQ molecule. They can be used to compute other thermodynamic energies according to the relationships of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamics in thermochemical field [40]. In the present study all thermodynamic calculations were done in gas phase and they could not be used in solution.

Table 4. Thermodynamic properties of MBMQ at different temperatures at B3LYP/6-311++G(d,p) level

T (K)	S (J/mol.K)	C (J/mol.K)	ΔH (kJ/mol)
100	383.18	125.23	8.12
200	495.94	211.22	24.88
298.15	597.42	304.16	50.12
300	599.3	305.94	50.69
400	700.21	398.51	85.99
500	797.99	478.36	129.95
600	891.19	543.7	181.17
700	979.13	596.78	238.29
800	1061.76	640.36	300.21
900	1139.33	676.58	366.11
1000	1212.24	707.03	435.34

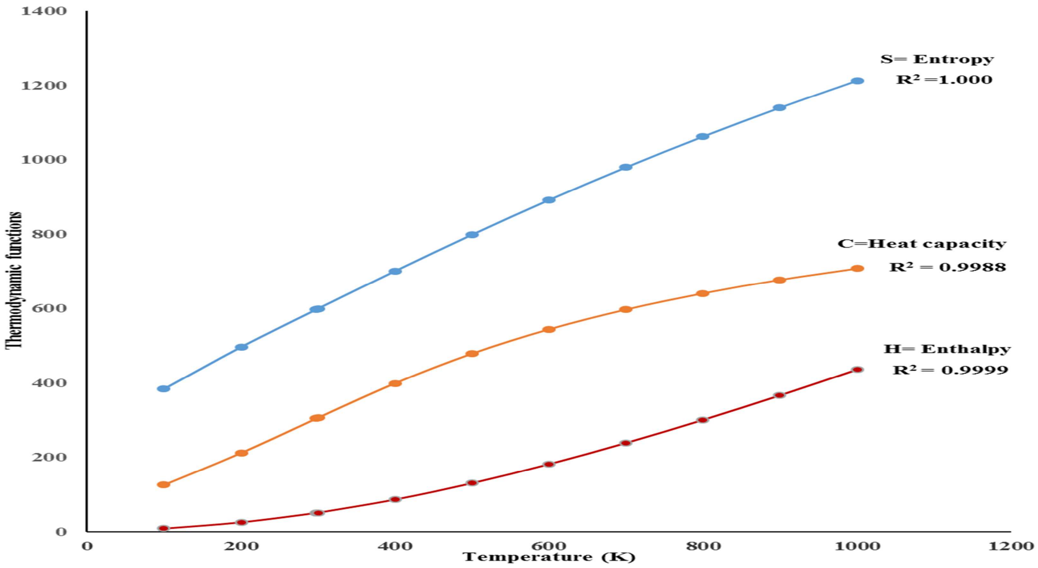


Fig. 6 Correlation graph between temperature and entropy, Heat capacity and enthalpy of MBMQ

CONCLUSION

In the present study, the optimized molecular structure, vibrational and electronic properties of the title compound have been calculated by DFT method B3LYP using 6-311++G(d,p) basis set. The computed vibrational wavenumbers were assigned and compared with experimental FT-IR and FT-Raman spectra. The experimental and calculated spectra are in good agreement and show a good frequency fit of the title molecule. The molecular electrostatic potential of MBMQ shows that this molecule has several possible sites for electrophilic and nucleophilic attack in which V(r) calculations provide insights into the order of preference. The calculated global reactivity descriptors of the title molecule may be used to understand the global nature of molecules in terms of their stability and it is possible to gain knowledge about the reactivity of molecules. Fukui function also helps in identifying the electrophilic and nucleophilic attacking sites within the molecule. The correlations between the statistical thermodynamic and temperature were also obtained. It is seen that the heat capacities, entropies and enthalpies increases with increasing temperature of molecule.

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