

# Synthesis, spectroscopic investigations and computational study of monomeric and dimeric structures of 2-methyl-4-quinolinol

Seied Ali Pourmousavi<sup>1,2</sup> · Ayoub Kanaani<sup>1</sup> · Fatemeh Ghorbani<sup>1</sup> · Kobra Khorsi Damghani<sup>1</sup> · Davood Ajloo<sup>1,2</sup> · Mohamad Vakili<sup>3</sup>

Received: 19 December 2014/Accepted: 28 April 2015 © Springer Science+Business Media Dordrecht 2015

Abstract The present study aimed to determine an efficient and solvent-free method to synthesize 2-methyl-4-quinolinol (2MQ, also known as 4-hydroxy-2methylquinoline) and includes spectroscopic investigations and computational studies. Molecular geometry and vibrational wavenumbers of 2MQ were investigated using the density functional (DFT/B3LYP) method with 6-311++G(d,p) and 6-311++G(2d,p) basis sets. According to calculations, the keto form of 2MQ is more stable than the annual form, and the dimeric conformation is predicted to be more stable than the monomeric conformations. A detailed analysis of the nature of the hydrogen bonding, using topological parameters such as electronic charge density, Laplacian, kinetic and potential energy density evaluated at the bond critical point, is also presented. The <sup>1</sup>H nuclear magnetic resonance chemical shifts of the molecule were calculated by the GIAO method. The molecule orbital contributions were studied by using total (TDOS) and partial (PDOS) density of states. The UV-visible spectrum of the compound was recorded and the electronic properties, such as HOMO and LUMO energies, were investigated by the time-dependent DFT (TD-DFT) approach. The linear polarizability ( $\alpha$ ) and the first-order hyperpolarizability ( $\beta$ ) values of the investigated molecule were computed using DFT quantum mechanical calculations. The results show that the 2MQ molecule may have a nonlinear optical comportment with non-zero values. The stability and charge delocalization of the molecule was studied by natural bond orbital analysis.

**Electronic supplementary material** The online version of this article (doi:10.1007/s11164-015-2084-4) contains supplementary material, which is available to authorized users.

Seied Ali Pourmousavi pourmousavi@du.ac.ir

<sup>&</sup>lt;sup>1</sup> School of Chemistry, Damghan University, 36716-41167 Damghan, Iran

<sup>&</sup>lt;sup>2</sup> Institute of Biological Sciences, Damghan University, 36716-41167 Damghan, Iran

<sup>&</sup>lt;sup>3</sup> Department of Chemistry, Ferdowsi University of Mashhad, 91775-1436 Mashhad, Iran

In addition, a molecular electrostatic potential map of the title compound was studied for predicting the reactive sites. Local reactivity descriptors, such as Fukui functions, local softness and electrophilicity indices analyses, were studied to determine the reactive sites within the molecule.

**Keywords** 2-Methyl-4-quinolinol  $\cdot$  DFT  $\cdot$  Hydrogen bonded dimer  $\cdot$  FT-IR  $\cdot$  <sup>1</sup>H NMR and UV spectra  $\cdot$  NBO analysis

## Introduction

Quinoline nucleus occurs in several natural compounds displaying a broad range of biological and pharmaceutical activity [1-3]. The synthesis of quinolone derivatives using a variety of methods has been documented [4-9].

We herein report the preparation of 2MQ by condensation of aniline with ethyl acetoacetate in the presence of sulfuric acid adsorbed silica gel ( $H_2SO_4$ -silica) under solvent-free conditions. The resulting enaminone system was subject to acid-catalyzed cyclization to yield 2MQ.

The present communication deals with structural, electronic and spectroscopic investigations of monomeric and dimeric forms of 2MQ, with the long-term objective of gaining better insight into such compounds. Particular attention has been focused on the effect of intermolecular N–H…O hydrogen bonding, on the bond distances, calculated frequencies and the nature of hydrogen bonding, by calculating topological parameters at the bond critical points using the atoms-in-molecule theory.

The aim of this work was to investigate the molecular structure and conduct a vibrational study of the molecule, due to its biological and pharmaceutical importance as analyzed by the density functional theory using 6-311++G(d,p) and 6-311++G(2d,p) basis sets. In order to obtain a description of the molecular vibrations of 2MQ, complete vibrational analysis has been carried out, providing detailed information about intramolecular vibrations in the entire mid-infrared region and especially in the fingerprint region. The ab initio quantum mechanical method is widely used for simulating IR and Raman spectra [10, 11].

The changes in electron density (ED) in the  $\sigma^*$  and  $\pi^*$  antibonding orbitals and stabilization energies  $E^{(2)}$  have been calculated by NBO analysis to acquire clear evidence of stabilization originating in the hyperconjugation of hydrogen-bonded interaction.

In this work, infrared (IR), <sup>1</sup>H nuclear magnetic resonance (NMR) and ultraviolet (UV)–Vis spectra of 2MQ are reported both experimentally and theoretically. Thermal stability of 2MQ was studied by thermo gravimetric analysis (TGA). HOMO and LUMO analyses have been used to elucidate information regarding charge transfer within the molecule. Molecular quantities, such as electronic chemical potential ( $\mu$ ), global hardness ( $\eta$ ), global softness (*S*), electronegativity ( $\chi$ ), electrophilicity indices ( $\omega$ ) and Fukui functions, are calculated and discussed. Moreover, molecular electrostatic potential (MEP) surface is plotted over the optimized geometry to elucidate the reactivity of the title compound. Reactive

nucleophilic and electrophilic sites in the MEP surface are compared with the fitting point charges to electrostatic potential. The standard thermodynamic functions, such as molecular energy (*E*), heat capacity  $(C_{p,m}^0)$ , entropy  $(S_m^0)$  and enthalpy  $(H_m^0)$ , are reported on the basis of vibrational analyses and statistical thermodynamics.

## Experimental

H<sub>2</sub>SO<sub>4</sub>-silica was prepared by our previously reported method [12]. All the reagents and chemicals were obtained from Merck and used without further purification. The development of reactions was monitored by thin-layer chromatography (TLC) on Merck pre-coated silica gel 60 F254 aluminum sheets, and visualized by UV light. IR spectra were recorded on a Shimadzu FT-IR 8300 Spectrophotometer using the KBr pellet technique. The FT-Raman spectrum of 2MQ in the solid phase was recorded employing a 180° back-scattering geometry and a Bomem MB-154 Fourier transform Raman spectrometer. It was equipped with a ZnSe beam splitter and a TE cooled InGaAs detector. Rayleigh filtration was afforded by two sets of two holographic technology filters. The spectra were accumulated for 1500 scans with a resolution of 2 cm<sup>-1</sup>. The laser power at the sample was 300 mW. <sup>1</sup>H NMR spectra was recorded at ambient temperature on a BRUKER AVANCE DRX-400 MHz spectrophotometer using CDCl<sub>3</sub> as the solvent and TMS as an internal standard. The ultraviolet absorption spectrum was examined in the range of 200-800 nm using a Perkin-Elmer lambda 25 recording spectrophotometer. TGA was recorded using a Perkin-Elmer model in order to determine its thermal stability. The analysis was carried out in an atmosphere of nitrogen at a heating rate of 25 °C per 10 min for the temperature range of 150-750 °C. Cyclic voltammetry measurements were performed by means of AUTOLAB PGSTAT20 potentiostatgalvanostat (EcoChemie, Netherlands). The electrochemical properties of 2MQ  $(c = 2 \times 10^{-3} \text{ M})$  were investigated by cyclic voltammetry with acetonitrile/0.1 M as the solvent in the presence of tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte, using Pt working and counter electrodes and Ag/AgCl as a reference electrode at ambient temperature (27 °C). Prior to the measurements, the solution was purged with argon to remove residual oxygen.

## Preparation of 2MQ using H<sub>2</sub>SO<sub>4</sub>-silica

To a mixture of a ethyl acetoacetate (1 mmol) and aniline (1.2 mmol),  $H_2SO_4$ -silica (0.15 g) was added. The mixture was stirred for 8 min at room temperature. After completion of the reaction, the reaction mixture was stirred in an oil bath at 140 °C, and TLC was used to monitor the progress of the reaction. At the end of the reaction, the resulting mixture was mixed with ethyl acetate and filtered to remove  $H_2SO_4$ -silica. The filtrate was washed with NaHCO<sub>3</sub> (3 × 7 mL) and then washed with water (5 mL), and the solvent was removed under reduced pressure to give the product, which was recrystallized from ethanol. After recrystallization from ethanol,

the 2MQ was obtained as a white solid. Yield: 67 %, <sup>1</sup>H-NMR (400 MHz, CDC1<sub>3</sub>): 11.75 (S, 1H, H<sub>a</sub>), 8.37–8.39 (d, J = 8 Hz, 1H, H<sub>e</sub>), 7.74–7.76 (d, J = 8 Hz, 1H, H<sub>b</sub>), 7.62–7.65 (t, J = 7.2 Hz, 1H, H<sub>c</sub>), 7.38–7.41 (t, J = 7.2 Hz, 1H, H<sub>d</sub>), 6.31 (S, 1H, H<sub>f</sub>), 2.52 (S, 3H. H<sub>g</sub>).

## Calculations

Geometry optimizations for the monomeric and dimeric forms of 2MQ were calculated at the B3LYP [13–15] level using 6-31G(d), 6-311G(d,p), 6-311++G(d,p), 6-311++G(2d,p), and LanL2DZ basis sets. All the calculations were performed using the Gaussian 03 W program package [16], with default convergence criteria and without any constraint on the geometry [17].

In this investigation, we observed that the calculated frequencies were slightly greater than the fundamental frequencies. These discrepancies are corrected either by computing anharmonic corrections explicitly [18], or by introducing a scale factor. In the present study, a selective scaling factor of 0.9961 was used for wavenumbers  $<1700 \text{ cm}^{-1}$  and 0.9556 was used for  $>1700 \text{ cm}^{-1}$  at 6-311++G(d,p); and 0.9963 was used for wavenumbers  $<1700 \text{ cm}^{-1}$  at 6-311++G(d,p); and 0.9963 was used for wavenumbers  $<1700 \text{ cm}^{-1}$  and 0.9959 was used for  $>1700 \text{ cm}^{-1}$  at 6-311++G(2d,p) [19]. The vibrational wavenumber assignments were carried out by combining the results of the GaussView 4.1.2 program [20] and the VEDA4 program [21]. The assignments of experimental frequencies are based on the observed band frequency and intensity changes in the infrared and Raman spectra, confirmed by establishing a one-to-one correlation between observed and theoretically calculated frequencies. For clear observation of these bands, band deconvolution techniques in the IR spectrum could be used. Lorentzian function was utilized for deconvolution of IR spectra using the Genplot package.

The nuclear magnetic resonance (NMR) chemical shift calculations were performed using the Gauge-Included Atomic Orbital (GIAO) method [22] in chloroform.

The time-dependent density functional theory (TD-DFT) was carried out to find electronic transitions. To calculate functional group contributions to the molecular orbitals, the total density of states (TDOS or DOS) the partial density of states (PDOS) spectra were prepared using the program GaussSum 2.2 [23]. NBO calculations [24] were performed using the NBO 3.1 program as implemented in the Gaussian 03 W package at the DFT/B3LYP level in order to understand intramolecular delocalization or hyperconjugation. The HOMO and LUMO were calculated by the B3LYP/6-311++G(2d,p) method. AIM 2000 software [25] was applied to obtain electron density at the hydrogen bond critical points, according to Bader's atoms in molecules (AIM) theory [26] at the B3LYP/6-311++G(d,p) and B3LYP/6-311++G(2d,p) levels.

The transition state (TS) structure of the photochromism reaction was obtained by using the QST3 method.

## **Results and discussion**

Noting recent reports on the use of sulfuric acid immobilized on silica ( $H_2SO_4$ -silica) [27–30] for various organic transformations, herein we wish to report an efficient procedure for the preparation of 2MQ in the presence of a catalytic amount of  $H_2SO_4$ -silica under solvent-free conditions.

The synthesis of 2MQ is outlined in Scheme 1. At first, condensation of aniline with ethyl acetoacetate gave the enaminone in the presence of  $H_2SO_4$ -silica at room temperature. In this reaction, enaminone was achieved in high yield. The resulting enaminone system was subject to acid-catalyzed cyclization under heating condition at 140 °C to yield 67 % 2MQ. In each case, the reaction was monitored by TLC and was discontinued when further consumption of the starting material was no longer observed.

The catalyst played a crucial role in the success of the reaction, in terms of time and yield. In the absence of the catalyst, the reaction of aniline with ethyl acetoacetate could be carried out, but the product was obtained in very low yield (10 %) after a prolonged reaction time.

The possibility of recycling the catalyst is one of the advantages of this procedure. The recovered catalyst was activated by heating at 100  $^{\circ}$ C under vacuum for 10 h, and was reused for the preparation of 2MQ. The recovered catalyst, after activation, was reused for four successive times without any appreciable loss in its activity.



Scheme 1 The synthesis of 2MQ

The present  $H_2SO_4$ -silica catalyzed procedure provides an efficient method for the preparation of 2MQ under thermal conditions. The significant advantages of this procedure are: (1) lower reaction temperature compared to the Cornad Limpach method (up to 250 °C [9]); (2) solvent-free conditions, (3)  $H_2SO_4$ -silica is an inexpensive, easily available and environmentally benign solid support acid that can be separated by simple filtration; and (4) the reusability of catalyst.

## **Geometrical parameters**

The compound can occur in two tautomeric forms, the enol and keto forms (Fig. 1). The two tautomeric monomer forms of 2MQ were subjected to geometry optimization at various levels of theory using the Gaussian03 package [16]. The energy difference between the keto and enol forms obtained from DFT method was 16.52 (calculated at the B3LYP/6-311++G(d,p) level) (see Table 1). According to all the calculations, the keto form of 2MQ was predicted to be more stable than the enol tautomer, and hence was used for theoretical investigations. Because of the hydrogen bonding formation, dimerization of 2MQ considerably reduces the energy, 52.7 kJ/mol (at the B3LYP/6-311++G(d,p)). These values indicate that the dimer form is quite stable in comparison to its monomeric form. The energy difference between dimer and keto forms suggests that there is a hydrogen bond in the dimeric form.



Fig. 1 a Tautomer equilibrium of 2MQ, b OH form and c NH form of the optimized structures obtained using B3LYP/6-311G(d,p) level

Calculation levels	E (enol)	E (keto)	$\Delta E$
B3LYP/6-31G(d)	-516.471676	-516.479090	19.45
B3LYP/6-311G(d,p)	-516.604319	-516.610419	16.00
B3LYP/6-311++G(d,p)	-516.613034	-516.619333	16.52
B3LYP/6-311++G(2d,p)	-516.627215	-516.632948	15.04
B3LYP/LanL2DZ	-516.390452	-516.404302	36.33

 Table 1
 The absolute total electronic energies (Hartree) and the energy differences of 2MQ at different basis sets

E absolute total electronic energies (Hartree);  $\Delta E$  energy differences between enol and keto at kJ/mol

The calculated optimized geometry parameters (bond lengths and bond angles) of 2MQ are compared in Table 2 with the experimental X-ray data of 2-(4fluorophenyl)quinolin-4(1H)-one [31], which is structurally similar to 2MQ. Taking into account that the molecular geometry in the vapor phase may be different from the solid base, owing to extended hydrogen bonding and stacking interactions, there is reasonable agreement between the calculated and experimental geometric parameters. When comparing the theoretical and the experimental bond lengths, the theoretical parameters are slightly deviated from the experimental data. For the title compound, it was found that the carbon-carbon bond lengths in the benzene ring were intermediates between typical C–C single (1.54 Å) and C=C double (1.34 Å) bonds. The greater bond length of  $C_3-C_4$  (1.405 Å) is due to delocalization of electron density due to the adjacent quinoline ring. According to an international crystallography table [32], the C=O bond length in the aromatic carboxylic group conforms to an average value of 1.226 Å. The experimental C=O bond length is 1.261 Å [33]. The calculated value of C=O (1.250 Å) in the 2MQ dimer reported in Table 2 is in good agreement with experimental data.

In crystal structure, the molecules are linked in centro-symmetric dimers by N– H…O hydrogen bonds [34]. The optimized molecular structure of the hydrogenbonded dimer is shown in Fig. 2. The computed bond lengths and bond angles of the dimer conformer differ slightly from the X-ray data. The strength of the H-bonds may also be found from the elongation of  $d_{X-H}(X = O, N \text{ or } F)$  and the red shifts of  $v_{XH}$ . The O…H distance in the hydrogen-bonded dimer is found to be 1.864 Å. The N–H and C=O distances involved in the hydrogen bonds are lengthened by 0.018 and 0.019 Å respectively upon dimerization. The N–H…O angle is calculated to be 174.11°, while the C=O…H angle is 127.58°.

#### Vibrational analysis

The title compound consists of 21 atoms, which have 57 normal modes. Those normal modes of 2MQ have been assigned according to the detailed motions of the individual atoms. Experimental Fourier transform infrared spectroscopy (FT-IR) and FT-Raman spectra, with corresponding theoretically simulated FT-IR and FT-Raman spectra for 2MQ, are shown in Figs. 3 and 4, respectively. The observed IR,

Parameters <sup>a</sup>	Monomer	Dimer	Exp. <sup>b</sup>	Parameters <sup>a</sup>	Monomer	Dimer	Exp. <sup>b</sup>
Bond lengths	(Å)						
$C_1 - C_2$	1.381	1.387	1.369	N <sub>15</sub> -C <sub>13</sub>	1.369	1.369	1.360
C <sub>2</sub> -C <sub>3</sub>	1.403	1.408	1.405	$C_4-C_9$	1.483	1.476	1.464
C <sub>3</sub> -C <sub>4</sub>	1.405	1.412	1.402	C <sub>9</sub> -O <sub>20</sub>	1.230	1.250	1.261
C <sub>4</sub> -C <sub>5</sub>	1.401	1.408	1.409	C <sub>9</sub> -C <sub>12</sub>	1.451	1.446	1.421
C5-C6	1.381	1.386	1.364	C <sub>12</sub> -C <sub>13</sub>	1.358	1.369	1.369
C <sub>6</sub> –C <sub>1</sub>	1.401	1.408	1.399	C <sub>12</sub> -H <sub>14</sub>	1.081	1.084	0.930
C <sub>3</sub> -N <sub>15</sub>	1.3843	1.387	1.379	C <sub>13</sub> -C <sub>16</sub>	1.500	1.503	_
N <sub>15</sub> -H <sub>21</sub>	1.008	1.027	0.898				
Bond angles	(°)						
$C_1 - C_2 - C_3$	119.6	119.51	119.4	$C_5 - C_4 - C_9$	120.8	121.07	121.9
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	120.4	120.43	120.4	$C_4 - C_3 - N_{15}$	119.1	119.01	120.0
C <sub>2</sub> -C <sub>3</sub> -N <sub>15</sub>	120.5	120.55	119.6	$C_4 - C_9 - C_{12}$	114.9	115.63	115.5
$C_3 - C_4 - C_5$	118.8	118.83	118.4	$C_4 - C_9 - O_{20}$	122.0	121.26	120.9
C <sub>3</sub> -C <sub>4</sub> -C <sub>9</sub>	120.4	120.10	119.7	C <sub>3</sub> -N <sub>15</sub> -H <sub>21</sub>	118.3	118.16	118.4
$C_4 - C_5 - C_6$	120.9	120.78	121.0	$C_3 - N_{15} - C_{13}$	122.8	122.99	121.9
C <sub>4</sub> -C <sub>5</sub> -H <sub>10</sub>	117.3	117.53	119.5	$C_9 - C_{12} - C_{13}$	122.5	122.17	122.9
C5-C6-H11	120.4	120.30	120.1	$C_9 - C_{12} - H_{14}$	117.6	118.37	118.6
C <sub>5</sub> -C <sub>6</sub> -C <sub>1</sub>	119.7	119.79	119.8	$C_{12}$ - $C_{13}$ - $C_{16}$	123.9	123.74	123.4
C <sub>6</sub> -C <sub>1</sub> -H <sub>7</sub>	119.7	119.93	119.5	$C_{13}$ - $C_{12}$ - $H_{14}$	119.9	119.45	118.6
$C_6 - C_1 - C_2$	120.6	120.66	121.0	N <sub>15</sub> -C <sub>13</sub> -C <sub>12</sub>	120.4	120.09	119.9
$C_1 - C_2 - H_8$	120.5	120.56	120.3	$N_{15} - C_{13} - C_{16}$	115.8	116.17	116.7
Intermoleculo	ar H bond len	gths					
N–H	_	1.027	0.898	О…Н	-	1.864	1.915
N–O	_	2.887	2.768	N–H–O	-	174.11	158.0
C=O	_	1.250	1.261	$C=O{\cdots}H$	-	127.58	139.9

Table 2 The optimized geometric parameters of 2MQ and comparison with experimental results, bond lengths in angstrom (Å) and bond angles in degrees (°)

<sup>a</sup> For atom numbering from Fig. 1

<sup>b</sup> Ref. [29]

Raman bands and calculated wavenumbers (scaled) and assignments are given in Table 3. A deconvoluted IR spectrum of 2MQ was depicted in Fig. S1. For complete vibrational analysis, the vibrational modes are discussed under five headings: (1) N–H group vibration, (2) C=O group vibration, (3) C–N vibration, (4) methyl group vibration, and (5) phenyl ring vibration.

## **N-H** group vibration

Intermolecular hydrogen bonding is simply revealed in the deviation of theoretical wavenumbers of N–H stretching modes. For heterocyclic compounds containing an N–H group, an N–H stretching band is observed in the 3500–3000 cm<sup>-1</sup> region, the



Fig. 2 Optimized dimer structure of 2MQ at B3LYP/6-311++G(2d,p) level



Fig. 3 FT-IR spectrum of 2MQ

position of which depends upon the degree of hydrogen bonding [35, 36]. In the present work, the theoretical calculation indicates that the scaled frequency value at  $3610 \text{ cm}^{-1}$  is assigned to N–H stretching vibrations. The PED that corresponds to this vibration is a pure mode with contribution of 100 %. The recorded spectra fail



Fig. 4 FT-Raman spectrum of 2MQ

to show such a band in the above-mentioned region, but it is observed at 3426 and  $3350 \text{ cm}^{-1}$  in FT-IR and FT-Raman spectrum as a medium band, and is assigned to N–H stretching vibrations. Two members of this class of compounds, which have been the subject of experimental studies, are 4-pyridone [37] and 2-pyridon [38]. By comparing this experimental property, the trend of hydrogen bond strength is obtained:

The N–H in-plane bending vibrations usually occur in the region of 1650–1580 cm<sup>-1</sup> [39]. The N–H in-plane bending vibrations are calculated at 1652, 1622, 1547 cm<sup>-1</sup>, and match well with the experimental FT-IR and FT-Raman peaks. The wavenumber obtained at 435 cm<sup>-1</sup> by FT-IR spectra and 438 cm<sup>-1</sup> by FT-Raman spectra are assigned to NH<sub>2</sub> out-of-plane bending vibrations. This assignment is in agreement with the literature [40].

## C=O group vibration

The appearance of strong bands in the FT-IR around 1800–1650 cm<sup>-1</sup> in aromatic compounds indicates the presence of a carbonyl group and is due to the C=O-stretching motion [41]. Formation of hydrogen bonding lowers the bond strength and thus v(C=O) absorption occurs at lower wavenumbers. The C=O stretching vibration of the 2MQ is observed at 1642, and 1627 cm<sup>-1</sup> in FT-IR and 1643 cm<sup>-1</sup> in FT-Raman spectrum, and these wavenumbers are in good coherence with the empirical value. The dominant in-plane C=O-bending vibration is calculated at 614 cm<sup>-1</sup>, in complete conformity with Rastogi et al. [42]. The bands recorded at 605 cm<sup>-1</sup> in FT-IR spectrum and 609 cm<sup>-1</sup> in FT-Raman spectrum are assigned to

<b>Table 3</b> ] 311++G(	Experimen 2d,p) level	tal [FT-IR s of theory	wavenumbe	ers (in cm	<sup>-1</sup> )] and th	neoretical [scaled	wavenumbers (	in $\text{cm}^{-1}$ )] of 2MQ at B3LYP/6-311++G(d,p) and B3LYP/6-
B3LYP/6-	·311++G(i	d,b)	B3LYP/6	-311++G(2	2d,p)	Experimental w	avenumber	
Freq	I.IR	${\rm A}_{\rm R}$	Freq	I.IR	${\rm A}_{\rm R}$	IR (neat)	R (neat)	Assignment (PED $\ge 10\%$ )
3464	55	94	3610	53	92	3426(6)	3350(4)	(001)HN <sup>0</sup>
3061	2	138	3202	2	135	3260(7)	3277(1)	${}^{\rm UC_{12}H_{14}(99)}$
3056	11	162	3196	10	157	3150(9)	3168(5)	$v_{\rm s} { m CH}_{ m ring}(95)$
3045	8	154	3185	8	157	3100(16)		$v_{a}CH_{ring}(96)$
3032	10	91	3172	10	90	3068(17)	3060(45)	$v_a CH_{ring}(94)$
3014	7	70	3153	7	70			$v_{a}CH_{ring}(99)$
2995	7	58	3132	7	58		2988(35)	$v_a CH_3(90)$
2933	12	100	3067	11	66	2908(30)	2920(30)	$v_{a}CH_{3}(100)$
2888	24	294	3022	22	293	2762(32)		$v_{s}CH_{3}(90)$
1686	468	106	1686	429	101	1642(49)	1643(16)	$\nu C = O(48), \ \nu C = C_{pyr}(19), \ \nu_a C C_{ring}(13)$
1650	67	34	1652	78	29	1627(13,sh)		$\nu C = O(32), \nu C = C_{pyr}(17), \delta NH(14), \nu_a C C_{ring}(13)$
1639	129	40	1643	126	42	1608(19,sh)	1610(28)	$v_a CC_{ring}(42), v_a CC_{pyr}(26)$
1617	10	31	1622	10	31	1597(52)	1596(37)	υ <sub>a</sub> CC <sub>ring</sub> (58), δNH(24)
1541	119	8	1547	105	8	1554(66)	1553(42)	δNH(24), δCH <sub>ring</sub> (22), υ <sub>a</sub> CC <sub>ring</sub> (20), υ <sub>a</sub> CNC(13)
1499	62	4	1508	69	4	1502(91)	1503(51)	δCH <sub>ring</sub> (22), υC <sub>3</sub> -N <sub>15</sub> (28), υ <sub>a</sub> CC <sub>ring</sub> (14), δ <sub>a</sub> CH <sub>3</sub> (14)
1480	19	21	1488	12	20	1471(42)	1473(39)	$\delta_a CH_3(64)$
1477	10	10	1483	6	8			$\delta_a CH_3(94)$
1452	60	4	1460	68	5	1446(11)		δCH <sub>ring</sub> (39), δ <sub>a</sub> CH <sub>3</sub> (33), υC-N(22)
1414	6	13	1422	7	12	1420(26)	1426(17)	δ <sub>s</sub> CH <sub>3</sub> (84)
1382	28	7	1389	25	1	1375(w)		$\delta NH(23)$ , $v_a C_9 - C_{12} = C_{13} - N_{15}(21)$ , $\delta C_{12} H_{14}(20)$ , $v_a C C_{ring}(11)$
1352	4	65	1354	7	64	1354(21)	1383(19)	$v_{a}CC_{ring}(76), \delta C_{12}H_{14}(22)$
1308	22	4	1316	20	7	1318(19)	1325(18)	$\delta_s CH_{ring}(26), \upsilon_a CC_{pyr}(26), \delta NH(13)$

Table 3	continued							
B3LYP/6	-311++G(i	(d,b	B3LYP/6	5-311++G(2	2d,p)	Experimental wa	avenumber	
Freq	I.IR	${\rm A_R}$	Freq	I.IR	$A_{R}$	IR (neat)	R (neat)	Assignment (PED $\ge 10\%$ )
1274	8	9	1280	10	5	1298(w,br)	1288(10)	$v_a C_5 - C_4 - C_3 - N_{15}(47), \delta_a CH_{ring}(36), \delta C_{12} H_{14}(11)$
1254	2	18	1259	1	19	1246(16)	1247(24)	$\nu C_{3}-N_{15}(46), \ \delta C_{12}H_{14}(24)$
1182	2	12	1188	2	12	1183(9)	1184(32)	δ <sub>a</sub> CH <sub>ring</sub> (35), υC-CH <sub>3</sub> (34), δC <sub>12</sub> H <sub>14</sub> (23)
1175	4	7	1181	4	3	1163(w)		$\delta_{\rm a} { m CH}_{ m ring}(74)$
1139	33	2	1145	30	2	1138(13)	1144 (19)	$\delta_{a}CH_{ring}(56), v_{s}C_{9}-C_{12}-C_{13}-N_{15}(36)$
1104	9	5	1110	L	5	1109(6)	1111(12)	$\delta CCC_{ring}(48), v_sC_4-C_9-C_{12}(26)$
1056	2	0	1065	2	0	1075(w,sh)		pCH <sub>3</sub> (88)
1047	7	31	1050	9	32	1044(w,sh)	1056(15)	Ring breathing(62)
1025	9	1	1033	L	1	1027(10)	1027(43)	pCH <sub>3</sub> (63)
1000	0	0	1002	10	3	992(w)	997(15)	δC <sub>12</sub> C <sub>13</sub> N <sub>15</sub> (56),υC-CH <sub>3</sub> (32)
866	11	3	666	0	0			$\gamma CH_{ring}(81)$
968	1	0	965	1	0	955(w)	933(11)	$\gamma { m CH}_{ m ing}(95)$
875	2	4	881	2	4	892(9,sh,br)	871(26)	δCCC <sub>ring</sub> (52), υCN(22)
863	1	0	871	12	0	865(w)		$\gamma CH_{ring}(48), \ \gamma C_{12}H_{14}(25), \ \gamma CC_{pyr}(23)$
852	27	0	859	17	0	847(14)		$\gamma C_{12} H_{14}(43), \gamma C H_{ring}(34)$
782	35	0	789	15	0	788(8)		$\gamma CH_{ring}(34), \ \gamma CC_{pyr}(32), \ \gamma C_{12}H_{14}(13)$
759	44	0	763	57	1	762(34)	756(45)	$\gamma CH_{ring}(86)$
757	3	5	761	ю	5	715(w,br)	704(13)	&CCC <sub>ring</sub> (47), &CCN(18)
675	ю	0	683	б	0	675(11)		$\gamma CCC_{ring}(27), \gamma C_{12}H_{14}(21), \gamma CH_{ring}(18)$
661	7	14	999	7	14	654(7)	653(77)	δCCC <sub>ring</sub> (64), υC-CH <sub>3</sub> (17)
588	ю	2	592	б	2	605(5)	609(21)	$\delta CO(27)$ , $\delta CCC_{ring}(20)$ , $\delta_{pyr}(20)$
583	19	1	591	18	1	585(8,sh)		$\gamma_{ m pyr}(67)$
551	3	17	554	ю	18	568(36)	567(100)	õCCC <sub>ring</sub> (45), õCCC <sub>pyr</sub> (39)

B3LYP/6	6-311++G(	(d,b)	B3LYP/6	5-311++G(	2d,p)	Experimental v	wavenumber	
Freq	I.IR	$A_{\rm R}$	Freq	I.IR	$A_{\rm R}$	IR (neat)	R (neat)	Assignment (PED $\ge 10\%$ )
526	0	0	528	0	0	538(4,br)		$\gamma \text{CCC}_{ m ring}(40),  \gamma_{ m pyr}(24)$
483	8	9	486	8	9	489(22)	490(63)	$\delta_{pyr}(47),  \delta_{ring}(14)$
452	54	0	439	3	9	442(11)		$\delta_{pyr}(37),  \delta_{ring}(16)$
436	3	9	437	51	0	435(7,sh)	438(41)	γNH(91)
431	1	0	434	0	0		406(28)	$\gamma \text{CCC}_{\text{ring}}(65)$
317	Ζ	1	319	7	1		325(38)	δC-CH <sub>3</sub> (40), δCO(35)
273	0	1	274	0	0		270(59)	$\gamma$ CCC <sub>ring</sub> (51), $\gamma_{pyr}(39)$
258	2	2	259	2	1		230(59)	$\tau_{\rm ting}(39), \ \delta \text{C-CH}_3(38)$
186	0	1	189	0	1			$\tau_{pyr}(40), \tau CH_3(17), \tau_{ring}(15)$
149	0	1	149	0	1			$\tau_{ m ting}(44), \ \gamma  m CO(34), \ \gamma  m CH_3(13)$
108	0	0	112	0	0			$\tau CH_3(83)$
93	ю	1	94	ю	1			$\tau_{ m ring}(56), \gamma_{ m pyr}(11)$
Freq vibr	ational wav	/enumber; ]	I.IR IR intens	sities in kM	/mol; AR. R	aman scattering ac	ctivities in A**4/	AM; experimental relative intensities are given in parenthesis; ring

phenyl ring; pyr pyridine; br broad; w weak; sh shoulder; s symmetric; a asymmetric; v stretching; δ in-plane bending; γ out-of-plane bending; ρ in-plane rocking; τ torsion

 $\delta$ CO of 2MQ. The C=O out-of-plane bending vibration is computed in the region 540  $\pm$  80 cm<sup>-1</sup> [43]. The predicted value at 149 cm<sup>-1</sup> is assigned to this vibration in 2MQ. According to the literature [44], this assigned value is in the expected range.

## C-N vibration

The C–N stretching frequency is a rather difficult task, since there are problems in identifying these frequencies from other vibrations [45]. Silverstein et al. [46] assigned C–N stretching vibrations in the region of 1386–1266 cm<sup>-1</sup> for aromatic amines. Bands at 1375, 1298, 1246, 1288, and 1247 cm<sup>-1</sup> in FT-IR and FT-Raman weres assigned to C=N stretching vibrations, respectively.

## Methyl group vibrations

The band at 2991 cm<sup>-1</sup> is assigned to CH<sub>3</sub> asymmetric stretching [47]. The C–H stretching in methyl groups occurs at lower frequencies than use of the aromatic ring (3100–3000 cm<sup>-1</sup>). In the present work, CH<sub>3</sub> asymmetric stretching is found at 2908 cm<sup>-1</sup> in FT-IR, and 2988, and 2920 cm<sup>-1</sup> in the Raman spectrum. CH<sub>3</sub> symmetric stretching is found at 2762 cm<sup>-1</sup> in FT-IR. In many molecules, the symmetric deformation appears with an intensity varying from medium to strong, and is expected in the range 1380 ± 25 cm<sup>-1</sup> [48]. According to our deconvolution results, the IR spectrum of 2MQ indicates the presence of one band. We observed the  $\delta_s$ CH<sub>3</sub> frequencies at 1420 cm<sup>-1</sup> (see Fig. S1) and at 1426 cm<sup>-1</sup> (FT-Raman). In FT-IR and FT-Raman, the bands observed at 1471, 1446 and 1473 cm<sup>-1</sup>, respectively, are assigned to the scissoring modes for the CH<sub>3</sub> group.

The rocking vibrations of CH<sub>3</sub> group are generally observed in the region 1070–1010 cm<sup>-1</sup> [49]. The bands at 1075 and 1027 cm<sup>-1</sup> in the IR spectrum and at 1027 cm<sup>-1</sup> (FT-Raman) are assigned as  $\rho$ CH<sub>3</sub> mode for the 2MQ. The twisting modes were not observed in the FT-IR, because they appear at very low frequency. The bands at 189 and 112 cm<sup>-1</sup> (B3LYP) are assigned as the twisting mode  $\tau$ CH<sub>3</sub>.

The calculated value of  $v(C-CH_3)$  was 666 cm<sup>-1</sup>. The experimentally observed value in the FT-IR spectrum at 654 cm<sup>-1</sup> confirms the assignment on comparison with the calculated value. In our present study, the strong bands at 325 and 230 cm<sup>-1</sup> in FT-Raman spectrum are assigned to  $\delta(C-CH_3)$ .

## Phenyl ring vibration

The phenyl ring spectral region chiefly involves C–H, C–C stretching, and C–C–C as well as H–C–C– bending vibrations. The bands due to the ring C–H stretching vibrations are observed as a collection of weak-to-moderate bands in the region of  $3100-3000 \text{ cm}^{-1}$ . The calculated wavenumbers for the CH-stretching modes were found in the range of  $3196-3153 \text{ cm}^{-1}$  and were matched with the experimental FT-IR and FT-Raman spectra. The PED for these modes suggested that these were pure modes. The aromatic C–H in-plane bending modes of benzene and its derivatives are observed in the region of  $1300-1000 \text{ cm}^{-1}$  [50, 51]. In our title molecule, weak

to medium bands observed in FT-IR as well as in FT-Raman spectrum at 1554–1138 and 1553–1144 cm<sup>-1</sup> are assigned to C–H in-plane bending vibrations for aromatic ring and show good agreement with computed wavenumbers by the B3LYP/6-311++G(2d,p) method. In the case of 2MQ, vibrations involving the C–H in-plane bending were found throughout the region of 1554–1138 cm<sup>-1</sup>. The C–H wagging (or out of bending vibrations) mode started appearing from 999 cm<sup>-1</sup> and had contribution up to 683 cm<sup>-1</sup> and was assigned well in the spectra. In general, the torsional modes appear in the low-wavenumber regions. In the present case, the calculated normal modes below 200 cm<sup>-1</sup> wavenumbers are mainly the torsional modes.

Generally, the C–C stretching vibrations in aromatic compounds give bands in the region of 1430–1650 cm<sup>-1</sup> [52]. In the present study, the frequencies observed in the FT-IR spectrum at 1608, 1597, 1554, and 1471 cm<sup>-1</sup> are assigned to C–C stretching vibrations. The same vibrations appear in the FT-Raman spectrum at 1610, 1596, 1553, and 1473 cm<sup>-1</sup>. All the rings stretching modes are expected to appear in the expected range. As expected, all the bands are observed with very weak and medium intensities. The C–C–C bending vibrations always occurred below 600 cm<sup>-1</sup> [53]. In our present study, strong bands observed in FT-IR spectrum at 715, 654 and 605 cm<sup>-1</sup> as weak bands, and 631, 406, and 270 cm<sup>-1</sup> as a medium to strong bands in FT-Raman spectrum, are assigned to C–C–C in-plane and out-of-plane bending vibrations, respectively.

## **NBO** analysis

Natural bond orbital (NBO) calculations were performed using the NBO 3.0 program as implemented in the Gaussian03 package at the DFT/B3LYP level. A useful aspect of the NBO is that it provides an accurate method for studying intramolecular and intermolecular bonding and interaction among bonds, and also gives an efficient basis for investigating charge transfer or conjugative interaction in various molecular systems [54]. In order to characterize the intramolecular and intermolecular interactions quantitatively, a second-order perturbation theory is applied that gives the energy lowering associated with such interactions. For each donor NBO (*i*) and acceptor NBO (*j*), the strength of interaction (or stabilization energy)  $E^{(2)}$  associated with electron delocalization between donor and acceptor is estimated by the second order energy lowering as in [55, 56].

For each donor (*i*) and acceptor (*j*) the stabilization energy  $E^{(2)}$  associated with the delocalization  $i \rightarrow j$  is determined as

$$E^{(2)} = \Delta E_{ij} = q_i \frac{(F_{ij})^2}{(E_i - E_i)^2}$$
(1)

where  $q_i$  is the donor orbital occupancy,  $E_i$  and  $E_j$  are diagonal elements, and  $F_{ij}$  is the off-diagonal NBO Fock matrix element.

The second-order perturbation theory analysis of the Fock matrix, in the NBO basis for 2MQ, calculated at B3LYP/6-311++G(2d,p) is presented in Table 4, which shows  $\pi$ -conjugation/resonance due to top-electron delocalization in ring,

Table 4 Selected second-	order perturbatio	in energies $E^{(2)}$ associated w	ith $i \rightarrow j$ delocalization in the ga	as phase for dim	er of 2MQ	
Donor (i) (occupancy)	ED <sub>A</sub> , % ED <sub>B</sub> , %	NBO hybrid orbitals	Acceptor (j) (occupancy)	ED <sub>A</sub> , % ED <sub>B</sub> , %	NBO hybrid orbitals	$E^{(2)}$ (kcal/mol)
$\pi(C_1-C_2)$	47.15	0.6867(sp <sup>1.00</sup> )C	$\pi^{*}(C_{3}-C_{4})$	52.85	0.7270(sp <sup>1.00</sup> )C	20.58
(1.72219)	52.85	0.7270(sp <sup>1.00</sup> )C	(0.42295)	47.15	-0.6867(sp <sup>1.00</sup> )C	
			$\pi^{*}(C_{5}-C_{6})$	52.98	0.7279(sp <sup>1.00</sup> )C	15.39
			(0.27305)	47.02	-0.6857(sp <sup>1.00</sup> )C	
$\pi(C_3-C_4)$	47.15	0.6867(sp <sup>1.00</sup> )C	$\pi^{*}(C_{1}-C_{2})$	52.85	0.7270(sp <sup>1.00</sup> )C	16.21
(1.61480)	52.85	0.7270(sp <sup>1.00</sup> )C	(0.30903)	47.15	-0.6867(sp <sup>1.00</sup> )C	
			$\pi^{*}(C_{5}-C_{6})$	52.98	0.7279(sp <sup>1.00</sup> )C	19.64
			(0.27305)	47.02	-0.6857(sp <sup>1.00</sup> )C	
			$\pi^*(C_{9}-O_{20})$	69.10	0.8313(sp <sup>1.00</sup> )C	20.15
			(0.2928)	30.90	-0.5558(sp <sup>1.00</sup> )O	
$\pi(C_5-C_6)$	47.02	0.6857(sp <sup>1.00</sup> )C	$\pi^{*}(C_{1}-C_{2})$	52.85	0.7270(sp <sup>1.00</sup> )C	22.85
(1.97989)	52.98	0.7279(sp <sup>1.00</sup> )C	(0.30903)	47.15	-0.6867(sp <sup>1.00</sup> )C	
			$\pi^{*}(C_{3}-C_{4})$	52.85	0.7270(sp <sup>1.00</sup> )C	17.45
			(0.42295)	47.15	-0.6867(sp <sup>1.00</sup> )C	
$\pi(C_{12}-C_{13})$	55.10	0.7423(sp <sup>1.00</sup> )C	$\pi^*(C_{9}-O_{20})$	69.10	0.8313(sp <sup>1.00</sup> )C	22.75
(1.81490)	44.90	0.6701(sp <sup>1.00</sup> )C	(0.2928)	30.90	-0.5558(sp <sup>1.00</sup> )O	
$LP_{1}(N_{15})$	I	sp1.00	$\pi^{*}(C_{3}-C_{4})$	52.85	0.7270(sp <sup>1.00</sup> )C	38.04
(1.99924)			(0.42295)	47.15	-0.6867(sp <sup>1.00</sup> )C	
			$\pi^*(C_{12}-C_{13})$	44.90	0.6701(sp <sup>1.00</sup> )C	41.97
			(0.2352)	55.10	-0.7423(sp <sup>1.00</sup> )C	
$LP_2(O_{20})$	I	${}^{1.00}$	$\sigma^{*}(C_{4}-C_{9})$	47.32	0.6879(sp <sup>2.16</sup> )C	19.53
(1.88993)			(0.06884)	52.68	-0.7258(sp <sup>2.00</sup> )C	
			$\sigma^{*}(C_{9}-C_{12})$	51.13	0.7151(sp <sup>1.86</sup> )C	17.90
			(0.0519)	48.87	-0.6991(sp <sup>1.99</sup> )C	

Table 4 continued						
Donor (i) (occupancy)	ED <sub>A</sub> , % ED <sub>B</sub> , %	NBO hybrid orbitals	Acceptor (j) (occupancy)	ED <sub>A</sub> , % ED <sub>B</sub> , %	NBO hybrid orbitals	$E^{(2)}$ (kcal/mol)
From monomer unit 1 to	unit 2					
$\sigma(C_{9}-O_{20})$	35.53	0.5961(sp <sup>2.22</sup> )C	$\sigma^{*}(N_{36}-H_{42})$	24.86	$0.4986(sp^{2.35})N$	0.18
(1.99444)	64.47	0.8029(sp <sup>1.52</sup> )O	(0.05480)	75.14	-0.8668(sp <sup>0.00</sup> )H	
$LP_1(O_{20})$	I	$(sp^{0.71})$	$\sigma^{*}(N_{36}-H_{42})$	24.86	0.4986(sp <sup>2.35</sup> )N	6.98
(1.96301)			(0.05480)	75.14	-0.8668(sp <sup>0.00</sup> )H	
$LP_{2}(O_{20})$	I	(s)(s)(s)(s)(s)(s)(s)(s)(s)(s)(s)(s)(s)(	$\sigma^{*}(N_{36}-H_{42})$	24.86	0.4986(sp <sup>2.35</sup> )N	13.30
(1.88224)			(0.05480)	75.14	-0.8668(sp <sup>0.00</sup> )H	
From monomer unit 2 to	unit I					
$\sigma(N_{36}\text{-}H_{42})$	75.14	0.8668(sp <sup>2.35</sup> )N	$\sigma^{*}(C_{9}-O_{20})$	64.47	0.8029(sp <sup>2.22</sup> )C	0.17
(1.98258)	24.86	$0.4986(sp^{0.00})H$	(0.01034)	35.53	$-0.5961(sp^{1.64})O$	

primary and secondary hyperconjugative interactions. The  $\pi$ -conjugation/resonance due to  $\pi$ -electron delocalization is involved due to the  $\pi \to \pi^*$  interactions, whereas the primary hyperconjugative interactions due to the various types of orbital overlaps such as  $\sigma \to \pi^*, \pi \to \sigma^*, n \to \sigma^*$ , and secondary hyperconjugative interactions due to the orbital overlap  $\sigma \rightarrow \sigma^*$ . The interactions  $\pi(C_1 - \sigma)$  $\pi(C_3 - C_4) \rightarrow \pi^*(C_1 - C_2,$  $C_2$ )  $\rightarrow \pi^*(C_3 - C_4, C_5 - C_6),$  $C_{5}-C_{6}$ and  $\pi(C_{5-})$  $C_6$ )  $\rightarrow \pi^*(C_1 - C_2, C_3 - C_4)$  are responsible for conjugation of respective  $\pi$ -bonds in phenyl ring. The electron density at the conjugated  $\pi$  bonds (1.97989–1.61480) of phenyl ring and  $\pi^*$  bonds (0.42295–0.27305) of phenyl ring indicate strong  $\pi$ electron delocalization within the ring, leading to a maximum stabilization of energy at 22.85 kcal/mol. The second-order perturbation theory analysis of Fockmatrix in NBO basis shows that strong intermolecular hyper-conjugative interactions are formed by orbital overlap between n(O) and n(N) with  $\pi^*(C_3-C_4)$ ,  $\pi^*(C_{12}-C_4)$  $C_{13}$ ,  $\pi^*(C_4-C_9)$  and  $\pi^*(C_9-C_{12})$  bond orbitals, which result in ICT causing stabilization of the system.

Second-order perturbation theory analysis of the Fock matrix in NBO basis: (1) from monomer unit 1 to unit 2, and (2) from monomer unit 2 to unit 1, is given in Table 4. In the dimer, the primary hyperconjugative interactions from the monomer unit (1) to the unit (2) due to  $n_1(O_{20})/n_2(O_{20}) \rightarrow \sigma^*(N_{36}-H_{42})$  stabilized the molecule up to 6.98 and 13.30 kcal/mol, and confirms the presence of classical interaction of  $N_{36}$ – $H_{42}$ ···O<sub>20</sub>.

#### **Charge distribution**

The calculation of atomic charges plays an important role in the application of quantum mechanical calculations to molecular systems [57]. The Mulliken [58] population analysis in the 2MQ molecule (monomer and dimer) is calculated using B3LYP level with 6-311++G(d,p) basis set as listed in Table S1. The plot of Mulliken atomic charge is shown in Fig. 5.

The charge distribution of the molecule has an important influence on the vibrational spectra. The charge distribution of 2MQ shows that the carbon atom



Fig. 5 Mulliken population analysis chart (monomer and dimer) of 2MQ



Fig. 6 The experimental <sup>1</sup>H NMR spectra of 2MQ

attached with hydrogen atoms is negative, whereas the remaining carbon atoms are positively charged. The high positive charge at C<sub>9</sub> is due to the effect of an oxygen atom attached to C<sub>9</sub>. Moreover, Mulliken atomic charges also show that the H<sub>21</sub> atom has more positive atomic charges than the other hydrogen atoms. This is due to the presence of an electronegative nitrogen atom (N<sub>15</sub>); the hydrogen atom (H<sub>21</sub>) attracts the positive charge from the nitrogen atom (N<sub>15</sub>). The presence of high negative charge on O atom and net positive charge on H atom may suggest the formation of intramolecular interaction in solid forms [59].

#### NMR spectrum

The <sup>1</sup>H NMR spectrum of the title compound was recorded in CDCl<sub>3</sub> (Fig. 6) and the chemical shifts are in good agreement with Ref. [5, 60]. An attached hydrogen or nearby electron-withdrawing atom or group can decrease the shielding and move the resonance of the attached proton towards a higher frequency. By contrast, an electron-donating atom or group increases the shielding and moves the resonance towards a lower frequency [61]. The geometry of the title compound, together with that of tetramethylsilane (TMS), is fully optimized. <sup>1</sup>H NMR chemical shifts are

Experiment	B3LYP/6- 311++G(d,p)	B3LYP/6- 31+G(d,p)	B3LYP/6- 311G(d,p)	pbepbe/6- 31+g(d,p)	Assignment
2.526	2.4321	2.37627	1.44073	2.2958	H(methyl) <sup>a</sup>
6.317	6.2404	7.2052	5.1525	6.2364	$H_{14}$
7.400	7.5682	7.5765	6.7385	7.5805	$H_8$
7.640	7.7769	7.7407	6.7205	7.7284	$H_{11}$
7.602	7.7928	7.8276	6.756	7.7940	$H_7$
8.389	8.6367	8.7048	7.5551	8.6148	$H_{10}$
11.752	9.6321	9.574	9.2692	9.5384	H <sub>21</sub>

Table 5 Experimental isotropic <sup>1</sup>H NMR chemical shifts of 2MQ in comparison with calculated theoretical values

<sup>a</sup> Mean value

calculated with the GIAO approach at B3LYP/6-311++G(d,p), B3LYP/6-31+G(d,p), B3LYP/6-311G(d,p) and pbepbe/6-31+g(d,p) levels [22]. The chemical shift of any 'X' proton  $(CS_x)$  is equal to the difference between isotropic magnetic shielding (IMS) of TMS and proton (x). It is defined by the equation:  $CS_X = -$ IMS<sub>TMS</sub> – IMS<sub>x</sub>. The experimental and calculated <sup>1</sup>H NMR chemical shifts ( $\delta$  in ppm) of 2MQ are given in Table 5. The chemical shifts of aromatic protons of organic compounds are usually observed in the range of 7.00-8.00 ppm, while the aliphatic protons resonance in the high field. The signals of the four aromatic protons (<sup>1</sup>H) of the title compound were theoretically calculated to be 7.5682-8.6367 ppm (B3LYP/6-311++G(d,p),and observed were at 7.400–8.389 ppm experimentally. We predicted  $H_{10}$  at 8.389 ppm in the lowest field, and H<sub>8</sub> at 7.400 ppm in the highest field of the aromatic region. The rotation of methyl groups causes their hydrogen atoms to show unique NMR peaks as well. The maximal deviation of chemical shifts obtained by B3LYP/6-311++G(d,p) (PCM) level is 2.120 for H<sub>21</sub>. The reason is that because of the electron withdrawing inductive effect of O, the activity of H<sub>21</sub> is increased, leading to formation of intermolecular hydrogen bonds, and making them difficult to predict.

#### Molecular electrostatic potential (MEP) surface

In order to investigate the chemical reactivity of the molecule, molecular electrostatic potential (MEP) surface is plotted over the optimized electronic structure of 2MQ using density functional B3LYP level with the 6-311++G(2d,p) basis set. The molecular electrostatic potential (MEP) surface is a plot of electrostatic potential mapped onto the constant electron density surface. The MEP surface is superimposed on top of the total energy density as a shell. A useful feature to study reactivity is that an approaching electrophile will be attracted to negative regions where the electron distribution effect is dominant. MEP is related to the electronic density and is a very useful descriptor in understanding sites for electrophilic and nucleophilic reactions as well as hydrogen bonding interactions [62].

Synthesis, spectroscopic investigations and computational...



Fig. 7 Molecular electrostatic potential surface (left) and the point charges, electric potential values (right) on an atom of 2MQ (for interpretation of the references to color in this figure, the reader is referred to the web version of the article). (Color figure online)

The negative (red) regions of MEP were related to electrophilic reactivity and the positive (blue) regions to nucleophilic reactivity. Figure 7 shows the computationally observed MEP surface map with the fitting point charges to the electrostatic potential V(r) for 2MQ. The different values of the electrostatic potential at the surface are represented by different colors. Potential increases in the order are red < orange < yellow < green < blue. The predominance of the light-green region in the MEP surface corresponds to a potential halfway point between the two extreme regions red and dark-blue color. The color code of the maps is in the range between -0.07107 a.u. (dark red) and 0.07107 a.u. (dark blue) in the compound, where blue indicates the strongest attraction and red indicates the strongest repulsion.

Gas ph	ase	Ethano	1	Aceton	itrile	In solvent major	Assignment	Experimental
$\lambda_{max}$ (nm)	(f)	$\lambda_{max}$ (nm)	(f)	$\lambda_{max}$ (nm)	(f)	contribution <sup>a</sup> ( $\geq 10 \%$ )		$\lambda_{abs}\;(nm)$
237.0	0.003	235.6	0.346	234.8	0.294	$H-3 \rightarrow L(50),$ $H-2 \rightarrow L(19),$	$n \rightarrow \sigma^*$	208
264.4	0.033	264.9	0.024	264.4	0.023	$H \rightarrow L+1(15)$ $H \rightarrow L(23),$ $H \rightarrow L+1(73)$	$\pi \to \sigma^*$	234
296.7	0.101	299.7	0.143	299.1	0.142	$H \to L(94)$	$n \to \pi^*$	320

**Table 6** Theoretical and experimental absorption wavelength  $\lambda_{max}(nm)$  and oscillator strengths (*f*) of 2MQ using TD-DFT/6-311G++(2d, p)

The average maximum negative and positive electrostatic potential values for these electrophilic and nucleophilic sites calculated at B3LYP/6-311++G(2d,p) are about -22.423 and -0.985 a.u. The fitting point charges to those potentials are -0.542 (O<sub>20</sub>) and 0.251 (H<sub>21</sub>). These sites give information about the region where the compound can have intermolecular interaction. The MEP map shows that the negative potential site is on electronegative atoms, and that the positive potential sites are around the hydrogen atom. The MEP provides a visual representation of the chemically active sites and the comparative reactivity of the atoms.

#### UV-Vis spectra and electronic properties

The UV-Vis spectral analysis of 2MQ was calculated by the TD-B3LYP/6-311++G(2d,p) method, and along with measured UV-Vis data, is summarized in Table 6. The UV-Vis spectra of 2MQ shown in Fig. 8 were measured in acetonitrile and ethanol solutions. GaussSum 2.2 program [23] has been used to calculate group contributions to the molecular orbitals and prepare the density of the state (DOS) as shown in Fig. 9. The DOS spectrum was created by convoluting the molecular orbital information with GAUSSIAN cures of unit height. DOS plot shows population analysis per orbital and demonstrates a simple view of the makeup of the molecular orbitals in a certain energy range. In Fig. 9, partial density of states (PDOS) has also been plotted, showing a percentage contribution of a group to each molecular orbital. The highest occupied molecular orbitals (HOMOs) and lowestlying unoccupied molecular orbitals (LUMOs) are named as Frontier molecular orbitals (FMOs). HOMO and HOMO-1 are the second highest and lowest unoccupied molecular orbitals LUMO and LUMO + 1, as shown in Fig. 10. The energy gap between the HOMO and LUMO orbital, which is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity, was calculated as 4.628 eV for the stable form of the title molecule. The HOMO shows that the charge density localized mainly on the carbonyl group, as LUMO is localized on the ring system.



Fig. 8 UV-Vis absorption spectra of 2MQ in different solvents



Fig. 9 DOS and PDOS plot of 2MQ

The calculated absorption wavelengths ( $\lambda_{max}$ ) and the experimental wavelengths, electron transition energies and oscillator strengths in the isolated gas phase, acetonitrile and ethanol phase (solvent) are listed in Table 6. The recorded UV–Vis spectrum shows three intense bands at 320, 234 and 208 nm. The maximum absorption wavelength corresponds to the electronic transition from HOMO  $\rightarrow$  LUMO (94 %) and HOMO  $\rightarrow$  LUMO (23 %), HOMO-  $\rightarrow$  LUMO + 1 (73 %) and HOMO-3  $\rightarrow$  LUMO (50 %), HOMO-2  $\rightarrow$  LUMO (19 %), HOMO  $\rightarrow$  LUMO + 1 (15 %) with contribution. The electronic absorption peak at 320 nm corresponds to the transition from the ground to the first excited state, and it is mainly described by one electron excitation from the HOMO  $\rightarrow$  LUMO (n  $\rightarrow \pi^*$ ). Moreover, lowering of the HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule.

The IP is defined as the minimum energy necessary to bring an electron from the material into a vacuum. In other words, ionization potentials (IP) are the energy difference between neutral molecules and the corresponding cationic systems. The electron affinity (EA) is defined as the first unoccupied energy level that injects electrons coming from a vacuum into where the material would occupy. In other words, EA is the energy difference between neutral molecules and the corresponding anionic systems. IP and EA are usually used to assess the energy barrier for the injection of holes and electrons [63]. Obviously, lower reorganization energy is necessary to achieve a high charge-transfer rate.



Fig. 10 The atomic orbital compositions of the frontier molecular orbital for 2MQ

Table 7	Electro chemical properties of the title compound	

Comp	$E_{\rm HOMO}/E_{\rm LUMO}^{\rm a}$	$IP^{a}$	$EA^{a}$	IP/EA <sup>a</sup>	$E^{\text{ox}}$ onset <sup>b</sup> (V)	$E_{\rm HOMO}/E_{\rm LUMC}^{\rm c}$
NH form OH form	-6.113/-1.485 -5.788/-1.436	7.865 8.047	1.290 0.896	7.865/1.290 8.047/0.896	1.439	5.839/1.211
OII Iolilli	5.7007 1.150	0.017	0.070	0.01//0.0/0		

<sup>a</sup> DFT/B3LYP calculated values

 $^b$  Oxidation potential in DMSO (2  $\times$   $10^{-3}$  mol  $L^{-1}$ ) containing 0.1 mol  $L^{-1}$   $Bu_4NBF_4$  with a scan rate of 100 mV  $s^{-1}$ 

<sup>c</sup>  $E_{\text{HOMO}}$  was calculated by  $E^{\text{ox}} + 4.4$  V, and  $E_{\text{LUMO}} = E_{\text{HOMO}} - \Delta E_{HL}$  [57]

Enol form has an IP of 8.047 eV (Table 7), which is bigger than that of the keto form (7.865 eV), indicating that the hole-transporting ability of keto is better than that of enol. On the other hand, the electron-transporting ability of a keto with an EA of 1.29 eV should be better than that of enol with an EA of 0.896 eV.

A cyclic voltammogram of supporting electrolyte is also shown in Fig. 11. The oxidation and reduction peaks are associated with the HOMO and LUMO levels, respectively. In the section that deals with experimental results, one should discuss EA



Fig. 11 Cyclic voltammogram of 2  $\times$   $10^{-3}$  M title compound. Scan rate 100 mV s  $^{-1}$ , electrolyte 0.1 M Bu\_4NBF\_4 in acetonitrile

and IP values rather than HOMO and LUMO levels, since the molecular orbitals energies are not observable but originate from quantum chemical approximations. Using cyclic voltammetry, the IP was estimated from the onset of the first oxidation peak, whereas EA is from the onset of the first reduction peak. The oxidation and reduction peaks are associated with the HOMO and LUMO levels, respectively. The HOMO energy level,  $E_H$ , was estimated from bellow equation [64]:  $E_{\text{HOMO}} = E^{\text{ox}} + 4.4$  V. The LUMO energy level,  $E_L$ , was obtained by adding the energy of the HOMO–LUMO gap,  $\Delta E_{HL}$ , to the  $E_H$  value, while the energy gap  $\Delta E_{HL}$  was determined from the difference between oxidation and reduction potentials. To bear a significant charge-transfer character is generally indicative of a HOMO/LUMO absorption transition. The HOMO/LUMO energy levels that are higher than those corresponding estimations from the experimental data may be related to various effects from conformation and solvents, which have not been taken into account here.

## Thermal analysis

Thermal analysis of 2MQ was carried out using a Perkin-Elmer model, simultaneous thermo gravimetric/differential thermal (TG/DT) analyzer. The sample was scanned in the temperature range of 150–750 °C at a rate of 25 °C for 10 min. The TG/DT curve is shown in Fig. 12. TGA-measurement showed that weight of the complex was constant up to 274 °C; thus, the complex did not contain crystallization water. The major weight loss (90 %) occurs between 274 and 376 °C. At temperatures above 400 °C, the sample weight was almost constant. In the differential thermal gravimetry (DTG) curve, one peak was identified at temperatures of 365 °C, indicating that the weight loss by thermal decomposition occurred in one step (Fig. 12b).

#### Prediction of hyperpolarizabilitie

Based on the finite-field approach, the non-linear optical parameters, such as dipole moment, polarizability, anisotropy polarizability and first order hyperpolarizability



Fig. 12 a TGA and b DTG curves of 2MQ

of 2MQ, are calculated using B3LYP level with 6-311++G(d,p) and 6-311++ G(2d,p) basis sets for more reliability. The numerical values of the above-mentioned parameters are listed in Table S2. Nonlinear optics deal with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wavenumber, phase, or other physical properties [65]. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a 3 × 3 × 3 matrix. The 27 components of the 3D matrix can be reduced to ten components due to the Kleinman symmetry [66]. The components of  $\beta$  are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the electric field is weak and homogeneous, this expansion becomes

$$E = E^{0} - \sum_{j} \mu_{i} F^{i} - \frac{1}{2} \sum_{ij} \alpha_{ij} F^{i} F^{j} - \frac{1}{6} \sum_{ij} \beta_{ijk} F^{i} F^{j} F^{k} - \frac{1}{24} \sum_{ijkl} \gamma_{ijkl} F^{i} F^{j} F^{k} F^{l} + \dots$$
(2)

where  $E_0$  is the energy of the unperturbed molecule,  $F^i$  is the field at the origin,  $\mu_i$ ,  $\alpha_{ij}$ ,  $\beta_{ijk}$ and  $\gamma_{ijkl}$  are the components of dipole moment, polarizability, the first hyperpolarizabilities, and second hyperpolarizabilities, respectively. The total static dipole moment, mean polarizability ( $\alpha_{tot}$ ), anisotropy polarizability ( $\Delta \alpha$ ) and the average value of the first hyperpolarizability ( $\langle \beta \rangle$ ) can be calculated using the following equations.

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{\frac{1}{2}}$$
(3)

$$\alpha_{tot} = \frac{1}{3} \left( \alpha_{xx} + \alpha_{yy} + \alpha_{zz} \right) \tag{4}$$

$$\Delta \alpha = \frac{1}{\sqrt{2}} \left[ \left( \alpha_{xx} - \alpha_{yy} \right)^2 + \left( \alpha_{yy} - \alpha_{zz} \right)^2 + \left( \alpha_{zz} - \alpha_{xx} \right)^2 + 6 \alpha_{xz}^2 + 6 \alpha_{xy}^2 + 6 \alpha_{yz}^2 \right]^{\frac{1}{2}}$$
(5)

$$\langle \beta \rangle = \left[ (\beta_{xxx} + \beta_{yyy} + \beta_{zzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \right]^{\frac{1}{2}}$$
(6)

Hyperpolarizabilities are very sensitive to the basis sets and levels of theoretical approach employed [67, 68], and the electron correlation can change the value of hyperpolarizability. It is already established that the molecular hyperpolarizability and mechanical stabilities get enhanced in organic molecules containing O–H and N–H groups, which are involved in hydrogen bond interactions [69]. Urea is one of the prototypical molecules used in the study of the nonlinear optical (NLO) properties of molecular systems. Therefore, it has frequently been used as a threshold value for comparative purposes.

The highest value of dipole moment is found along  $\mu_y$ . In this direction, the value is equal to -6.327 D. For directions X and Z, the values are equal to 1.232 and 0.001 D, respectively, as shown in Table S2. Total polarizability ( $\alpha_{tot}$ ) calculated as  $-10.187 \times 10^{-24}$  and  $-10.166 \times 10^{-24}$  esu for title molecule. The first hyperpolarizability values ( $\langle \beta \rangle$ ) of the title compound are equal to  $56.642 \times 10^{-31}$  and  $55.600 \times 10^{-31}$  esu for 2MQ. Theoretically, the first hyperpolarizability for title compound are 15.19 and 14.91 times the magnitude, respectively, of the standard NLO material urea ( $\mu$  and  $\beta$  of urea are 1.372 D and 0.3728  $\times 10^{-30}$  esu). Our title molecule, with a greater dipole moment and hyperpolarizability value than urea, shows that the molecule has large NLO optical property.

#### Thermodynamic functions

On the basis of vibrational calculation at the B3LYP/6-311++G(2d,p) level of theory, the standard statistical thermodynamic functions of heat capacity  $(C_{n,m}^0)$ ,

entropy  $(S_m^0)$ , enthalpy  $(H_m^0)$  and molecular energy (E) for the title compound were obtained from the theoretically calculated frequencies listed in Table S3. It can be observed that these thermodynamic functions increase with temperature ranging from 100 to 800 K, due to the fact that the molecular vibrational intensities increase with temperature [70]. The corresponding quadratic equations obtained by B3LYP/ 6-311++G(2d,p) are as follows, and the related figure is shown in Fig. 13.

For 2MQ by B3LYP/6-311++G(2d,p)

$$C_{p,m}^{o} = 0.4287 + 0.1596T - 7 \times 10^{-5}T^{2} \quad (R^{2} = 0.9992)$$

$$S_{m}^{o} = 52.522 + 0.1547T - 3 \times 10^{-5}T^{2} \quad (R^{2} = 1)$$

$$H_{m}^{o} = 1.6339 + 0.0684T - 1 \times 10^{-4}T^{2} \quad (R^{2} = 0.9999)$$

$$E = 104.100 + 0.0087T - 5 \times 10^{-5}T^{2} \quad (R^{2} = 0.9997) \quad (7)$$

All the thermodynamic data supply helpful information for the further study of 2MQ. 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 a thermo chemical field [71, 72]. Note that all thermodynamic calculations were done in gas phase and they could not be used in solution.

The values of some thermodynamic parameters [such as zero-point vibrational energy (ZPVE), thermal energy, specific heat capacity, rotational constants, rotational temperature and entropy] of the title compound are listed in Table S4. The variation in ZPVE seems to be significant. The ZPVE is much higher by the



Fig. 13 Correlation graph of thermodynamic properties and temperatures by B3LYP/6-311++G(2d,p) for 2MQ molecule

B3LYP/6-311++G(d,p) level than by the B3LYP/6-311++G(2d,p) level. The total energies are found to decrease with the increase of the basis set dimension.

#### **Reactive descriptors of 2MQ**

#### Global reactivity parameters

The energies of frontier molecular orbitals ( $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ ), energy band gap ( $E_{\text{HOMO}}$ - $E_{\text{LUMO}}$ ), electronic chemical potential ( $\mu$ ), electron negativity ( $\chi$ ), global hardness ( $\eta$ ), global softness (S), electrophilicity indices ( $\omega$ ) and dipole moment (D) [73] of 2MQ are listed in Table 8. On the basis of  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ , these are calculated by using the below equations.

$$\mu = \frac{1}{2} (E_{\text{HOMO}} + E_{\text{LUMO}}) \tag{8}$$

$$\chi = -\mu = -\frac{1}{2}(E_{\text{HOMO}} + E_{\text{LUMO}}) \tag{9}$$

$$\eta = \frac{1}{2} (E_{\text{HOMO}} - E_{\text{LUMO}}) \tag{10}$$

$$S = \frac{1}{2\eta} \tag{11}$$

$$\omega = \frac{\mu^2}{2\eta} \tag{12}$$

The chemical hardness is quite useful in explaining the chemical stability. The molecules having a large HOMO–LUMO energy gap will be more stable and less reactive than soft molecules having a small HOMO–LUMO energy gap. From Table 8, the total energy of the NH form is lower than that of the OH form, while chemical hardness of the NH form is greater than that of the OH one, which indicates that the NH form of the title compound is more stable than its OH form in the gas phase. In additional, in order to evaluate the solvent effect on the above-mentioned properties of the title compound, we carried out calculations in four kinds of solvent (Hexane, dichloromethane, Ethanol and acetonitrile) with the B3LYP/6-311++G(2d,p) level using the PCM model, and the results are given in Table 8. From Table 8, we can conclude that the total molecular energies obtained by the PCM method decrease with the increasing polarity of the solvent. Solvent effects improve the charge delocalized in the molecules, therefore inducing the dipole moments to be raised.

According to these results, the stability of the title compound increases in going from the gas phase to the solution phase.

The usefulness of this new reactivity quantity has recently been demonstrated in understanding the toxicity of various pollutants in terms of their reactivity and site

5						
	Gas (OH)	Gas (NH)	Hexane (NH)	CH <sub>2</sub> Cl <sub>2</sub> (NH)	EtOH (NH)	CH <sub>3</sub> CN (NH)
$E_{ m total}$ (hartree)	-516.627215	-516.632948	-516.638506	-516.646974	-516.649064	-516.649448
$E_{ m HOMO}$ (eV)	-5.788	-6.113	-6.144	-6.221	-6.243	-6.248
$E_{\rm HOMO-1}$ (eV)	-6.919	-6.452	-6.583	-6.812	-6.874	-6.886
$E_{\rm LUMO}~(eV)$	-1.436	-1.485	-1.523	-1.611	-1.635	-1.639
$E_{LUMO+1}$ (eV)	-0.766	-0.741	-0.754	-0.810	-0.826	-0.827
EHOMO-LUMO gap (eV)	-4.352	-4.628	-4.621	-4.610	-4.608	-4.609
Chemical potential $(\mu)$	3.612	3.799	3.834	3.916	3.939	3.944
Global hardness $(\eta)$	2.176	2.314	2.311	2.305	2.304	2.305
Global softness (S)	0.460	0.432	0.433	0.434	0.434	0.434
Elecronegativity $(\chi)$	-3.612	-3.799	-3.834	-3.916	-3.939	-3.944
Electrophilisity indices $(\omega)$	2.998	3.118	3.180	3.326	3.367	3.374
Dipole moment (D)	2.516	6.445	7.447	9.129	9.565	9.637

Table 8 Calculated energy values of 2MQ by B3LYP/6-311++G(2d,p) basis set

selectivity [74–76]. The computed electrophilicity index of 2MQ describes the biological activity of drug–receptor interaction.

#### Local reactivity descriptors

The most relevant local descriptor of reactivity is the Fukui function, the derivative of the electronic chemical potential with respect to the external potential due to the compensating nuclear charges in the system. For a system of N electrons, independent calculations are to be made for corresponding N +1, N -1 and N, which are the total electrons present in anion, cation and neutral state of molecules, respectively. The Muilliken population analysis yields gross charges, and for all atoms, *k*. In a finite-difference approximation, the condensed Fukui functions are given by the equations:

For nucleophilic attack 
$$f_k^+ = q_k(N+1) - q_k(N)$$
 (13)

For electrophilic attack 
$$f_k^- = q_k(N) - q_k(N-1)$$
 (14)

For free radical attack 
$$f_k^0 = \frac{1}{2} [q_k(N+1) - q_k(N-1)]$$
 (15)

The condensed-to-atom quantity,  $\omega_k^{\alpha}$  corresponding to local electrophilisity index,  $\omega(r)$ , was obtained as described previously [77]

$$\omega_k^{\alpha} = \omega f_k^{\alpha} \tag{16}$$

where  $\alpha =+, -$ , and 0 refer to nucleophilic, electrophilic and free radical reactions, respectively. Fukui functions: local softness and local electrophilicity indices for selected atomic sites in 2MQ are listed in Table S5. The reactivity orders for the nucleophilic attack: the reactivity of C<sub>3</sub> in the substitution was found to have a loss in 2MQ at 6-311++G(2d,p) level. The nucleophilic reactivity order was C<sub>3</sub>>C<sub>13</sub> at the 6-311++G(2d,p) and 6-311++G(d,p) basis set on 2MQ. On the other hand, the reactivity order for the electrophilic case was O<sub>20</sub>>C<sub>4</sub>>C<sub>12</sub>>N<sub>15</sub>>H<sub>11</sub>>H<sub>7</sub>>H<sub>8</sub>>-H<sub>21</sub>>C<sub>6</sub>>C<sub>5</sub>>H<sub>10</sub>>H<sub>19</sub>>H<sub>18</sub>>H<sub>17</sub>>C<sub>2</sub>>C<sub>16</sub>>C<sub>1</sub>>C<sub>9</sub>>C<sub>13</sub>>C<sub>3</sub> at the 6-311++G(2d,p) basis set on 2MQ. If one compares the three kinds of attacks, it is possible to observe that the electrophilic attack shows more reactivity in comparison with the free radical and nucleophilic case.

#### **Topological parameters**

One of the most useful implements to characterize atomic and molecular interactions, particularly hydrogen bonding, is the topological analysis using 'Atoms in molecules' (AIM) theory [26]. According to AIM theory, any chemical bond, including hydrogen bonding, is characterized by the existence of bond critical points (BCP). After the bond, critical points have been localized, and several properties can be calculated at their position in space. Amongst these,  $\rho_{BCP}$  or the charge density at the bond critical point is of chief importance. Laplacian of the



Fig. 14 Molecular graphs of 2MQ dimer, *red points* indicate the bond critical points (BCPs) between bonded atoms. (Color figure online)

charge density at the bond critical point,  $\nabla^2 \rho_{BCP}$  and the ellipticity are two derived quantities. The latter provides a measure of the magnitude to which charge is favorably accumulated in a given plane. It has been observed that for closed-shell interactions, as found in ionic bonds, hydrogen bonds, and van der Waals molecules,  $\nabla^2 \rho_{\text{BCP}}$  should be positive (in the range 0.015–0.15 a.u) and  $\rho$  low (0.002–0.040 a.u.). The values mentioned here are according to Koch and Popelier criteria [78], based on AIM theory. A molecular graph of the timer is shown in Fig. 14. As indicated, in addition to usual bonds, the molecular graphs indicate a BP and a BCP between nitrogen and hydrogen, which confirms that there is an intramolecular hydrogen bond (H-bond) in these molecules. Interestingly, each BCP contains a wealth of chemical information that properly describes the nature of the corresponding chemical bond. The values of electron density,  $\rho_{\rm BCP}$ , Laplacian of electron density,  $\nabla^2 \rho_{BCP}$ , kinetic energy density, G<sub>BCP</sub>, potential energy density,  $V_{\rm BCP}$ , and electronic energy density at the BCP are the parameters that are usually used to characterize a chemical bond. Topological parameters for hydrogen bonds in dimer are given in Table 9. The  $\rho_{BCP}$  values obtained in the present study and positive magnitude of  $\nabla^2 \rho_{BCP}$  reported in Table 9 are on the high side of the requirements to define a hydrogen bond, and thus a strong interaction may be concluded. The energy of N-H...O hydrogen bond can be calculated using the relationship  $E_{\text{HB}} = V(r_{\text{BCP}})/2$  as described by Espinosa et al. [79]. In case of the 2MQ dimer,  $E_{\rm HB}$  has been calculated to be 7.15372 kcal/mol by B3LYP/6-311++G(d,p) and 7.08365 kcal/mol B3LYP/6-311++G(2d,p) methods. The characteristics of the intermolecular hydrogen bonding can also be estimated by the energetic properties of BCP associated with the interaction. The ratio  $G/\rho_{\rm BCP}$ may be used to define the character of the interaction, where G is kinetic energy

Parameters	N–H…O (BCP)	
	d,p <sup>a</sup>	2d,p <sup>b</sup>
Electron density	0.0309 a.u.	0.0309 a.u.
Laplacian of electron density	0.02213 a.u.	0.02282 a.u.
Lagrangian kinetic energy $G(\mathbf{r})$	0.02247 a.u.	0.02270 a.u.
Hamiltonian kinetic energy $K(\mathbf{r})$	-0.00033 a.u.	-0.00012 a.u.
Potential energy density $V(\mathbf{r})$	-0.02280 a.u.	-0.02258 a.u.
H-bond energy	7.15372 kcal/mol	7.08365 kcal/mol

Table 9 Topological parameters for Hydrogen bonded interactions

<sup>a</sup> B3LYP/6-311++G(d,p)

<sup>b</sup> B3LYP/6-311++G(2d,p)

density and is always positive. This ratio may be larger than 1.0 for closed shell (hydrogen bonding, ionic bonds and van der Waals interaction) [26]. The ratio  $G/\rho_{\rm BCP}$  in the present study is 0.727, which is close to 1.0 for the hydrogen bonding. Similar results (with  $G/\rho_{\rm BCP}$  value slightly lower than 1.0) have been stated for extraordinarily strong hydrogen bonding in other compounds [80, 81].

#### Transition state and kinetic

The transition state (TS) structure of tautomer equilibrium was obtained to use the QST3 method. It fully optimized structures for TS from calculations at B3LYP/6-311++G(d,p) level of theory, as shown in Fig. S2. TS structures were identified by the existence of a single imaginary frequency in normal-mode results. The imaginary frequency implied that TS is a saddle point on the potential surface.

Frequency calculations allowed the obtaining of thermodynamic quantities in order to estimate activation parameters. The imaginary frequency that characterizes the TS is mainly associated with the hydrogen transfer from  $O_{20}$  to the  $N_{15}$ . After the analysis of vibration frequencies for optimized geometry, the standard molar enthalpies, entropies and Gibbs free energies were obtained at different temperatures, and some of the results are given in Table 10. The first order rate constant k(T) was calculated using the transition state theory TST [75]. It was assumed that the transmission coefficient is equal to 1 as in the following equation:

$$K(T) = \left(\frac{K_B T}{h}\right) \exp\left(-\frac{\Delta G^{\#}}{RT}\right)$$
(20)

where  $\Delta G^{\#}$  is the Gibbs free energy change between the reactant and the transition state and  $k_{\rm B}$ , *h* are the Boltzmann and Plank constants, respectively.  $\Delta G^{\#}$  was calculated using the following relations:

$$\Delta G^{\#} = \Delta H^{\#} - T \Delta S^{\#} \tag{21a}$$

where  $\Delta H^{\#}$  is

e compound from B3LYP/6-311G(d,p) calculations	d
(P) for the title	
in state (TS) and product	
es of reactant (R), transition	ST
ar enthalpies, entropie	
The standard moli	R
Table 10	Temn (K)

Temp (K)	R		TS		Ρ	
	$S$ (cal mol <sup>-1</sup> $K^{-1}$ )	H (kcal mol <sup>-1</sup> )	$S (cal mol^{-1} K^{-1})$	H (kcal mol <sup>-1</sup> )	$S$ (cal mol <sup>-1</sup> $K^{-1}$ )	H (kcal mol <sup>-1</sup> )
250	89.38	-323964.10	89.58	-323904.73	90.64	-323960.91
300	96.22	-323962.21	96.22	-323902.91	97.80	-323959.02
350	102.97	-323960.02	102.81	-323900.76	104.29	-323956.82
400	109.63	-323957.52	109.35	-323898.32	110.99	-323954.31
450	116.17	-323954.75	115.78	-323895.58	117.56	-323951.51

Temp (K)	ΔS <sup>#</sup> (J/mol K)	$\Delta H^{\#}$ (kJ/mol)	$\Delta G^{*}$ (J/mol)	Rate constant $(cm^3 molecule^{-1} s^{-1})$	-log (k)	1000/T	Slope	Activation energy (kcal mol <sup>-1</sup> )
250	0.861	248.140	247924.892	8.25663E-40	39	4.000	13.069	59.8
300	0.029	247.899	247889.769	4.31665E-31	30	3.333		
350	-0.677	247.694	247931.360	7.28749E-25	24	2.857		
400	-1.195	247.487	247965.448	3.46922E - 20	19	2.500		
450	-1.613	247.308	247953.117	1.37901E-16	16	2.222		

Table 11 Gas phase rate constants in different temperatures

$$\Delta H^{\#} = V^{\#} + \Delta Z P V E + \Delta E(T)$$
(22b)

 $V^{\#}$  is the potential energy barrier and  $\Delta ZPVE$  and  $\Delta E(T)$  are the differences of ZPVE and temperature corrections between the TS and the reactant, respectively. Entropy values were estimated from vibrational analysis. To further understand how the temperature affected the reaction, rate constants were computed in the temperature range of 250–450 K. The values of activation energy were obtained from the plots of calculated ( $-\log k$ ) versus 1000/*T* (Fig. S3).  $\overline{E_a}$  was obtained from the slope of the cited plot and the data are presented in Table 11. By increasing the temperature, the rate constant increased too. When the temperature changed from 250 to 450 K, *k* increased approximately  $10^{23}$  times.

One of the ways to get the most stable tautomer is to calculate the tautomeric equilibrium constant,  $K_{eq}$ , which is readily calculated from the Gibb's free energy via  $K_{eq} = e^{-\Delta G/RT}$ , where  $\Delta G$  is the change in Gibb's free energy between products and reactants at temperature *T*, and *R* is the ideal gas constant [82]. The  $\Delta G$  value at the B3LYP/6-311++G(2d,p) level is predicted to be 42.206 kJ/mol between keto and enol tautomers of the title compound. The  $K_{eq}$  is computed as 3.997 × 10<sup>-8</sup> at 298.15 K for keto↔enol tautomerization. This observation indicates that the direction of equilibrium is in favor of the keto structure.

### Conclusion

we developed an efficient method for the synthesis of 2MQ using  $H_2SO_4$ -silica as a green, reusable, inexpensive and easily available catalyst. Then the calculated geometric parameters, vibrational wavenumber, frontier molecular orbitals, molecular electrostatic potential surfaces and the nonlinear properties of 2MO using DFT/B3LYP method were discussed. The theoretical results were compared with the experimental vibrations. The present work also explores the nature of intermolecular hydrogen bonding interaction between the monomeric forms of 2MQ with the help of topological parameters. The NBO analysis indicates the intramolecular charge transfer between the bonding and antibonding orbitals. The predicted NLO properties of the title compound are much greater than those of urea. TD-DFT calculations starting from optimized geometry were carried out in both gas and solution phase to calculate excitation energies of the title compound. The title compound is chemically stable up to 274 °C. The MEP map shows that the negative potential sites are on electronegative atoms, while the positive potential sites are around the hydrogen atoms. These sites give information about the region from where the compound can have noncovalent interactions. The tautomeric equilibrium constant is computed as  $3.997 \times 10^{-8}$  at 298.15 K for keto  $\leftrightarrow$  enol tautomerization of the title compound. We hope this article will be helpful for the design and synthesis of new materials.

Acknowledgments Financial support of Damghan University is acknowledged. The authors also wish to extend thanks to Prof. Jamroz for providing VEDA4 software.

#### References

- R.D. Larsen, E.G. Corley, A.O. King, J.D. Carrol, P. Davis, T.R. Verhoeven, P.J. Reider, M. Labelle, J.Y. Gauthier, Y.B. Xiang, R.J. Zamboni, J. Org. Chem. 61, 3398 (1996)
- 2. Y.L. Chen, K.C. Fang, J.Y. Sheu, H.S.L. Su, C.C. Tzeng, J. Med. Chem. 44, 2374 (2001)
- 3. M.P. Maguire, K.R. Sheets, K. Mcvety, A.P. Spada, A. Zilberstein, J. Med. Chem. 37, 2129 (1994)
- G. Jones, A.R. Katritzky, C.W. Ress, *Comprehensive Heterocyclic Chemistry*, vol. 5 (Pergamon, New York, 1996), p. 167
- 5. V. Nadaraj, S.T. Selvi, Indian J. Chem. 46B, 1203 (2007)
- 6. S.B. Sapkal, K.F. Shelke, B.B. Shingate, M. S. J. Korean Chem. Soc. 54, 723 (2010)
- 7. S. Yuan, K. Zhang, J. Xia, Asian J. Chem. 25, 5535 (2013)
- A. Nilsen, G.P. Miley, I.P. Forquer, M.W. Mather, K. Katneni, Y. Li, S. Pou, A.M. Pershing, A.M. Stickles, E. Ryan, J.X. Kelly, J.S. Doggett, K.L. White, D.J. Hinrichs, R.W. Winter, S.A. Charman, L.N. Zakharov, I. Bathurst, J.N. Burrows, A.B. Vaidya, M.K. Riscoe, J. Med. Chem. 57, 3834 (2014)
- 9. M. Conrad, L. Limpach, Ber. 20, 944 (1887)
- M. Vakili, S.F. Tayyari, A. Kanaani, A.-R. Nekoei, S. Salemi, H. Miremad, A.R. Berenji, R.E. Sammelson, J. Mol. Struct. 998, 99 (2011)
- 11. A. Kanaani, D. Ajloo, H. Kiyani, M. Farahani, J. Mol. Struct. 1063, 30 (2014)
- 12. S.A. Pourmousavi, S.S. Kazemi, Monatsh. Chem. 143, 917 (2011)
- 13. A.D. Becke, J. Chem. Phys. 98, 5648 (1993)
- 14. C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37, 785 (1988)
- 15. B. Miehlich, A. Savin, H. Stoll, H. Preuss, Chem. Phys. Lett. 157, 200 (1989)
- 16. M.J. Frisch et al., Gaussian 03, Revision C.01 (Gaussian, Inc., Wallingford, 2004), p. 255
- 17. H.B. Schlegel, J. Comput. Chem. 3, 214 (1982)
- 18. A.P. Scott, L. Radom, J. Phys. Chem. 100, 16503 (1996)
- 19. M. Karabacak, M. Cinar, M. Kurt, Spectrochim. Acta A 74, 1197 (2009)
- 20. R. Dennington, T. Keith, Millam Gaussview Version 5 (Semichem Inc., Shawnee Mission KS, 2009)
- 21. M.H. Jamroz, Vibrational Energy Distribution Analysis: VEDA 4 Program (Warsaw, Poland, 2004)
- 22. K. Wolinski, J.F. Hilton, P. Pulay, J. Am. Chem. Soc. 112, 8251 (1990)
- 23. N.M. O'Boyle, A.L. Tenderholt, K.M. Langer, J. Comput. Chem. 29, 839 (2008)
- E.D. Glendening, A.E. Reed, J.E. Carpenter, F. Weinhold, NBO Version 3.1 (Gaussian Inc, Pittsburgh, 2003)
- 25. F.W. Biegler-König, J. Schönbohm, D. Bayles, J. Comp. Chem. 22, 545 (2001)
- 26. R.W.F. Bader, Atoms in Molecules. A Quantum Theory (Oxford University Press, New York, 1990)
- 27. B. Mukhopadhyay, Tetrahedron Lett. 47, 4337 (2006)
- 28. V.K. Rajput, B. Mukhopadhyay, Tetrahedron Lett. 47, 5939 (2006)
- 29. B. Roy, B. Mukhopadhyay, Tetrahedron Lett. 48, 3783 (2007)
- 30. V.K. Rajput, B. Roy, B. Mukhopadhyay, Tetrahedron Lett. 47, 6987 (2006)
- 31. M.J. Mphahlele, A.M. El-Nahas, J. Mol. Struct. 688, 129 (2004)
- 32. F.H. Allen, Acta Crystallogr. B 58, 380 (2002)
- 33. M.J. Mphahlele, A.M. El-Nahas, J. Mol. Struct. 688, 129 (2004)
- 34. H.T. Flakus, A. Miros, P.G. Jones, J. Mol. Struct. 604, 29 (2002)
- 35. S. Gunasekaran, R. Thilak kumar, S. Ponnusamy, Spectrochim. Acta A 65, 1041 (2006)
- 36. I.L. Tocan, M.S. Woolley, J.C. Otero, J.I. Marcos, J. Mol. Struct. 470, 241 (1998)
- 37. H.T. Flakus, A. Tyl, Vib. Spectrosc. 63, 440 (2012)
- 38. H.T. Flakus, A. Tyl, A. Maslankiewicz, J. Phys. Chem. A 115, 102 (2011)
- 39. S. Arjunan, S. Mohan, Spectrochim. Acta A 72, 436 (2009)
- 40. J.C. Evans, Spectrochim. Acta A 16, 428 (1960)
- 41. J. Mohan, Organic Spectroscopy-Principle and Applications, 2nd edn. (Narosa Publishing House, New Delhi, 2000)
- V.K. Rastogi, M.A. Palafox, K. Lang, S.K. Singhal, R.K. Soni, R. Sharma, Indian J. Pure Appl. Phys. 44, 653 (2006)
- 43. N.P.G. Roeges, A Guide to the Complete Interpretation of Infrared Spectra of Organic Structure (Wiley, New York, 1994)
- 44. V. Balachandran, K. Parimala, Spectrochim. Acta A 102, 30 (2013)
- 45. N. Sundaraganesan, H. Saleem, S. Mohan, M. Ramalingam, V. Sethuraman, Spectrochim. Acta A 62, 740 (2005)

- M. Silverstein, G.C. Basseler, C. Morill, Spectrometric Identification of Organic Compounds (Wiley, New York, 1981)
- 47. G. Socrates (ed.), Infrared Characteristic Group Frequencies (Wiley, England, 1980)
- 48. R.M. Silverstein, G.C. Basseler, C. Morill (eds.), Spectroscopic Identification of Organic compounds (Wiley, New York, 1981)
- 49. T. Kupka, R. Wrzalik, G. Pasterna, K. Pasterny, J. Mol. Struct. 616, 17 (2002)
- 50. V. Arjunan, S. Sakiladevi, T. Rani, C.V. Mythili, S. Mohan, Spectrochim. Acta A 88, 220 (2012)
- 51. M. Karabacak, D. Karagoz, M. Kurt, Spectrochim. Acta A 72, 1076 (2009)
- 52. V. Krishnakumar, N. Surumbakuzhali, Spectrochim. Acta A 71, 1810 (2009)
- 53. G. Gunasekaran, E. Sailatha, Indian J. Pure Appl. Phys. 47, 259 (2009)
- M. Snehalatha, C. Ravikumar, I.J. Hubert, N. Sekar, V.S. Jayakumar, Spectrochim. Acta A 72, 654 (2009)
- 55. M. Szafran, A. Komasa, E.B. Adamska, J. Mol. Struct. (Theochem) 827, 101 (2007)
- 56. J. Choo, S. Kim, H. Joo, Y. Kwon, J. Mol. Struct. (Theochem) 587, 1 (2002)
- 57. R. Meenakshi, Mol. Simul. 36, 425 (2010)
- 58. R.S. Mulliken, J. Chem. Phys. 23, 1833 (1995)
- 59. L. Xiao-Hong, L. Xiang-Ru, Z. Xian-Zhou, Comput. Theor. Chem. 969, 27 (2011)
- 60. T. Sakamoto, Y. Kondo, D. Uchiyama, H. Yamanaka, Tetrahedron 47, 5111 (1991)
- 61. N. Subramania, N. Sundaraganesan, J. Jayabharathi, Spectrochim. Acta A 76, 259 (2010)
- 62. E. Scrocco, J. Tomasi, Adv. Quantum Chem. 11, 115 (1978)
- 63. X. Li, X. Liu, Z. Wu, H. Zhang, J. Phys. Chem. A 112, 11190 (2008)
- 64. H.-Y. Wang, L.-F. Chen, X.-L. Zhu, C. Wang, Y. Wan, H. Wu, Spectrochim. Acta A 121, 355 (2014)
- 65. M.E. Casida, K.C. Casida, D.R. Salahub, Int. J. Quantum Chem. 70, 933 (1998)
- 66. D.A. Kleinman, Phys. Rev. 126, 1977 (1962)
- 67. H. Sekino, R.J. Bartlett, J. Chem. Phys. 84, 2726 (1986)
- 68. J. Henriksson, J. Saue, P. Norman, J. Chem. Phys. 128, 24105 (2008)
- 69. S. Debrus, H. Ratajczak, J. Venturini, N. Pincon, J. Baran, J. Barycki, T. Glowiak, A. Pietraszko, Syn. Metals **127**, 99 (2002)
- 70. M.A. Palafox, Int. J. Quantum Chem. 77, 661 (2000)
- 71. J. Bevan Ott, J. Boerio-goates, *Calculations from Statistical Thermodynamics* (Academic Press, Waltham, 2000)
- 72. R. Zhang, B. Dub, G. Sun, Y. Sun, Spectrochim. Acta A 75, 1115 (2010)
- 73. J. Padmanabhan, R. Parthasarathi, V. Subramaniaan, P.K. Chattaraj, J. Phys. Chem. A 111, 1358 (2007)
- 74. R. Parthasarathi, J. Padmanabhan, V. Subramanian, B. Maiti, P.K. Chattraj, J. Phys. Chem. A 107, 10346 (2003)
- 75. R. Parthasarathi, J. Padmanabhan, V. Subramanian, B. Maiti, P.K. Chaltraj, Curr. Sci. 86, 535 (2004)
- 76. R. Parthasarathi, J. Padmanabhan, V. Subramanian, U. Sarkar, B. Maiti, P.K. Chattraj, Internet Electron. J. Mol. Des. 2, 798 (2003)
- 77. R.G. Parr, W. Yang, J. Am. Chem. Soc. 106, 4049 (1984)
- 78. U. Koch, P.L.A. Popelier, J. Phys. Chem. 99, 9747 (1995)
- 79. E. Espinosa, E. Molins, C. Lecomte, Chem. Phys. Lett. 285, 170 (1998)
- 80. D.E. Hibbs, J. Overgaard, R.O. Plitz, Org. Biomol. Chem. 1, 1191 (2003)
- 81. M.T. Caroll, C. Chang, R.F.W. Bader, Mol. Phys. 63, 387 (1988)
- 82. S.W. Paine, A. Salam, Chem. Phys. 331, 61 (2006)