# Journal of Molecular Structure 1063 (2014) 30-44

Contents lists available at ScienceDirect

# Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

# Synthesis, spectroscopic investigations and computational study of 4-((9,10-dioxo-9,10-dihydroanthracen-1-yl)oxy)benzaldehyde

A. Kanaani<sup>a</sup>, D. Ajloo<sup>a,b,\*</sup>, H. Kiyani<sup>a,\*</sup>, M. Farahani<sup>a</sup>

<sup>a</sup> School of Chemistry, Damghan University, Damghan, Iran

<sup>b</sup> Department of Physical Chemistry, School of Chemistry, College of Science, University of Tehran, Tehran, Iran

#### HIGHLIGHTS

#### GRAPHICAL ABSTRACT

- Synthesis 4-((9,10-dioxo-9,10dihydroanthracen-1yl)oxy)benzaldehyde for the first time.
- IR, <sup>1</sup>H NMR <sup>13</sup>C NMR, UV spectra and NBO analysis were reported.
- The first order hyperpolarizability and HOMO, LUMO energy gap are theoretically predicted.
- Thermodynamic properties and their correlations with temperature have been obtained.
- Transition structures were calculated by QST3 approach and yielded the potential energy surfaces.

#### ARTICLE INFO

Article history: Received 31 October 2013 Received in revised form 23 December 2013 Accepted 15 January 2014 Available online 23 January 2014

Keywords: Photochromism Density functional theory Spectroscopy NBO QST3



# $A \hspace{0.1in} B \hspace{0.1in} S \hspace{0.1in} T \hspace{0.1in} R \hspace{0.1in} A \hspace{0.1in} C \hspace{0.1in} T$

The molecular structure, vibrational frequencies, corresponding vibrational assignments of 4-((9,10dioxo-9,10-dihydroanthracen-1-yl)oxy)benzaldehyde in *"trans*" and *"ana"* forms have been investigated by UV–Vis, FT-IR and NMR spectroscopy as well as density functional theory (DFT) B3LYP method with 6-311++G(d,p) basis set. The vibrational analysis of the two forms of cited compound was performed by means of infrared absorption spectroscopy in combination with theoretical simulations. The obtained geometrical parameters and wavenumbers of vibrational normal modes from the DFT method were in good consistency with the experimental values. The <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) chemical shifts of the molecule were calculated by GIAO method. Computed molecular orbital and time dependent DFT oscillator renderings agree closely with experimental observations. The stability of the molecule arising from hyper-conjugative interaction and charge delocalization has been analyzed using NBO analysis. In order to predict the reactive sites, a molecular electrostatic potential map (MEP) for the title compound was obtained. Transition structures were calculated by QST3 and IRC methods which yielded the potential energy surface and activation energy.

© 2014 Elsevier B.V. All rights reserved.

# 1. Introduction

Photochromism is characterized by photo-induced reversible isomerization of one isomer to another isomer which has a different absorption spectrum. Photochromic materials are potentially useful for advanced optoelectronic devices such as rewritable optical memory, optical switching, ophthalmic lenses, dental filling materials, chemical sensing, and color displays [1–3]. Among the different categories of photochromic materials, aryloxyanthraquinone (AAQ) derivatives have greatly considered due to their outstanding exclusive properties such as low fatigue, bi-stability, and small thermal interconversion at ambient conditions [4]. The





<sup>\*</sup> Corresponding authors. Address: School of Chemistry, Damghan University, Damghan, Iran. Tel.: +982325235431 (D. Ajloo).

E-mail addresses: ajloo@du.ac.ir (D. Ajloo), hkiyani@du.ac.ir (H. Kiyani).

photochromic reaction of AAQs involves photoinduced reversible aryl group migration process. The "*trans*" quinone isomer undergoes photochemical rearrangement of the  $\pi$ -bond system to form the "*ana*"-quinone isomer upon irradiation with UV light (Scheme 1) [5–7]. It was found that this process is photochemically and thermally reversible, as well as represents a new type of photochromic reaction of substituted AQs [8–10]. Also, photochemical migration of hydrogen, or acyl groups from *trans*-quinoid to the *ana*-quinoid structure was investigated [9–10]. Stability of "*ana*" and "*trans*" forms at ambient temperature is required for technical application of aryloxyquinones [11,12]. Natural and synthetic 9,10-AQs show a wide spectrum of biological activities [13–16].

The theoretical *ab initio* and normal coordinate analysis give information regarding to the nature of the electronic structure, the functional groups, orbital interactions and mixing of skeletal frequencies. The structural characteristics and vibrational spectroscopic analysis of title compound by the quantum mechanical ab initio and DFT methods have not been studied. Thus, extensive experimental and theoretical studies were carried out on "trans" and "ana" forms to obtain a complete, reliable and accurate vibrational assignments and structural characteristics of the compound. Ab initio quantum mechanical method is widely used for simulating IR spectrum [17,18]. Time-dependent DFT (TD-DFT) calculations have also been used for the analysis of the electronic spectrum and spectroscopic properties. The energies, degrees of hybridization, populations of the lone electron pairs of nitrogen, energies of their interaction with the anti-bonding  $\pi^*$  orbitals, electron density (ED) distributions and  $E^{(2)}$  energies have been calculated by NBO analysis using DFT method to give clear evidence of stabilization originating from the hyperconjugation of various intra-molecular interactions. In this work, IR, <sup>1</sup>H, <sup>13</sup>C NMR parameters and UV-Vis spectrum of "trans" and "ana" forms are reported experimentally and theoretically.

Theoretically calculated HOMO and LUMO energies are closely associated to oxidation potentials and reduction potentials of molecules. As stated by Koopman's theorem [19], ionization energy is equal to the HOMO energy of a molecule, but of opposite sign, with the consequence that oxidation potentials may be related to HOMO energies. The electron located in the HOMO orbital is removed during oxidation. In a similar way LUMO energy is related to reduction potentials. Both HOMO and LUMO energies may readily be calculated, i.e. by means of DFT and other computational methods, as extensively discussed elsewhere [20].



Scheme 1. Photochromic reaction of aryloxyanthraquinones (AAQs).

There has been growing interest in using organic materials for nonlinear optical (NLO) devices, functioning as second harmonic generators, frequency converters, electro-optical modulators, etc. Since the second order electric susceptibility is related to first hyperpolarizability, the search for organic chromophores with large first hyperpolarizability is fully justified. The organic compounds showing high hyperpolarizability are those containing an electron donating or withdrawing group interacting through conjugated double bonds. Consequently, the present work thought interesting to examine the potential energy surface (PES) at the DFT level of theory in order to obtain the kinetic and thermodynamic parameters as well as reasonable understanding the conversion of "*trans*" and "*ana*" forms in gas phase.

# 2. Experimental

The mid-IR spectra were recorded in the 4000–400 cm<sup>-1</sup> region with spectral resolution of  $2 \text{ cm}^{-1}$  by averaging the results of 16 scans on a Perkin–Elmer RXI Fourier Transform spectrophotometer using KBr pellet technique (solid phase). The ultraviolet absorption spectrum was examined in the range of 200-800 nm using Perkin-Elmer lambda 25 recording spectrophotometer. The photoinduced (rans) form was formed upon UV irradiation (Hg lamp DRSh-260+ UV-transmitting glass filters). Cyclic voltammetry measurements were performed by means of AUTOLAB PGSTAT20 potentiostatgalvanostat (EcoChemie, Netherlands). The electrochemical properties of title compound ( $c = 2 \times 10^{-3}$  M) was investigated by cyclic voltammetry with CH<sub>2</sub>Cl<sub>2</sub> as the solvent in the presence of 0.1 M Bu4NBF4 as the supporting electrolyte using Pt working and counter electrodes and Ag/AgCl as reference electrode at ambient temperature [21]. Prior to the measurements the solution was purged with argon to remove residual oxygen. The NMR spectra were recorded for trans form at ambient temperature on a Brucker AVANCE DRX 400 MHz using CDCl<sub>3</sub> as solvent. Melting point was measured on a Buchi 510 melting point apparatus and is uncorrected. Chemicals were obtained from Merck and Fluka and used without further purification. The development of reaction was monitored by thin layer chromatography (TLC) analysis on silica gel 60 GF<sub>254</sub> aluminum sheets, using ethyl acetate:petroleum ether (1:3) as mobile phase. The spots were exposed by UV light and iodine vapor.

# 2.1. Synthesis of 4-((9,10-dioxo-9,10-dihydroanthracen-1-yl)oxy) benzaldehyde (3) (Scheme 2)

The starting 1-dichloroanthraquinone 1 (2.77 g, 10 mmol) and 4-hydroxybenzaldehyde 2 (2.8 g, 11 mmol) were dissolved in 30 mL of dry *N*,*N*-dimethylformamide (DMF) in round bottom flask, followed by addition of dry  $K_2CO_3$  (6.9 g, 49.9 mmol) while the solution was stirred at reflux. Stirring was continued for 36 h at reflux conditions. After completion of the reaction, it was monitored by TLC, solvent was evaporated under vacuum and water added to



Scheme 2. Synthesis of 4-((9,10-dioxo-9,10-dihydroanthracen-1-yl)oxy)benzaldehyde (3).

the residue. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and purified by flash column chromatography on silica gel to give 2.53 g (70%) of compound 3 as a pale orange solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) ( $\delta$ /ppm): 9.95 (s, 1H), 8.28–8.33 (m, 2H), 8.17–8.19 (m, 1H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.81–7.90 (m, 1H), 7.76–7.80 (m, 2H), 7.49 (d, *J* = 8.0, 1H), 7.09 (d, *J* = 8.8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 190.7 182.5, 181.4, 162.9, 154.3, 136.0, 135.4, 134.5, 134.3, 134.0, 132.6, 132.1, 131.5, 129.2, 127.4, 127.0, 125.3, 125.1, 116.7; UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ /nm: 270, 330 before irradiation and 270, 330, 475 after irradiation.

## 2.2. Calculations

All quantum calculations were performed using the Gaussian03 package [22] program. The geometry of "trans" and "ana" forms was fully optimized without any constraint in the potential energy surface at HF/6-311G(d,p) method. This geometry was then reoptimized again at B3LYP/6-311++G(d,p) [23] method. Cartesian coordinate for "trans", "ana" and transition state forms calculated by B3LYP/6-311G++(d,p) method were listed in Tables S1-S3. Harmonic vibrational wavenumbers were calculated using the analytic second derivatives to confirm the convergence to minima on the potential surface. Assignment of the calculated wavenumbers was aided by the animation option of the GAUSSVIEW program, which gives a visual presentation of the vibrational modes [24]. The assignments of the experimental frequencies are based on the observed band frequency and intensity changes in the infrared spectra confirmed by establishing one to one correlation between observed and theoretically calculated frequencies. However, the vibrational frequency values computed at these levels contain known systematic errors [25]. The DFT hybrid B3LYP functional methods tend to overestimate the fundamental mode and so scaling factor of 0.9613 has to be used for obtaining a considerably better agreement with experimental data [25]. Lorentzian function has been utilized for deconvolution of IR spectra using the Genplot package [26].

The nuclear magnetic resonance (NMR) chemical shifts calculations were performed using Gauge-Included Atomic Orbital (GIAO) method [27] at B3LYP/cc-pVTZ level and the <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced to the corresponding values for TMS, which



Fig. 1. Optimized geometry by B3LYP/6-311++G(d,p) for (a) "trans" and (b) "ana" quinone.

was calculated at the same level of theory. The characterization of excited states and electronic transitions were performed using the time-dependent DFT method (TD-B3LYP) on their corresponding optimized ground state geometry. We used the time-dependent

#### Table 1

Selected geometric (B3LYP) parameters of "trans" and "ana" forms, atom labeling according to Fig. 1.

Parameters	"trans"	"ana"	Parameters	"trans"	"ana"
Bond lengths (Å)			Bond lengths (Å)		
C <sub>3</sub> C <sub>4</sub>	1.4037	1.4105	C <sub>8</sub> -C <sub>9</sub>	1.4964	1.3784
C <sub>4</sub> —C <sub>5</sub>	1.3988	1.4044	C=022	1.2185	1.2282
C <sub>5</sub> C <sub>6</sub>	1.3895	1.3888	C9-C10	1.4138	1.4526
C <sub>6</sub> C <sub>1</sub>	1.3982	1.3966	C <sub>10</sub> -C <sub>7</sub>	1.4987	1.4913
C <sub>3</sub> C <sub>7</sub>	1.4851	1.4852	C <sub>14</sub> —C <sub>15</sub>	1.3927	1.4674
C <sub>4</sub> -C <sub>8</sub>	1.4955	1.4607	C-O <sub>24</sub>	1.3780	1.3593
C7=023	1.2198	1.2216	O <sub>24</sub> —C <sub>25</sub>	1.3721	1.3827
Bond angles (°)			Bond angles (°)		
A(3, 4, 8)	121.9	120.1	A(3, 7, 23)	121.5	121.5
A(4, 8, 9)	117.6	122.7	A(10, 7, 23)	120.7	122.1
A(8, 9, 10)	120.2	118.8	A(9, 10, 11)	121.0	120.6
A(9, 10, 7)	121.7	121.5	A(4, 8, 0)	120.1	113.3
A(10, 7, 3)	117.8	116.4	A(9, 8, 0)	122.2	124
A(7, 3, 4)	120.7	120.5	A(9, 15, O)	122.6	123.4
			A(14, 15, O)	116.2	120.5
Dihedral angles (°)			Dihedral angles (°)		
D(1, 2, 3, 7)	-179.8	179.6	D(5, 4, 8, 22)	1.4	0.5
D(2, 3, 4, 8)	179.3	179.4	D(6, 5, 4, 8)	-179.5	-179.8
D(2, 3, 7, 23)	-1.0	-1.4	D(11, 10, 7, 23)	2.3	2.7
D(2, 3, 7, 10)	178.6	177.9	D(14, 15, 9, 8)	-177.8	179.6
D(3, 4, 8, 22)	-177.9	-179.9	D(15, 9, 8, 4)	177.2	172.5
D(4, 3, 7, 23)	179.0	177.8	· · · ·		

density functional theory (TD-DFT), which is found to be an accurate method for evaluating the low-lying excited states of molecules and has been thoroughly applied to solve physical and chemical problems. Moreover, molecular electrostatic potential (MEP) surface was plotted over the optimized geometry to elucidate the reactivity of "*trans*" and "*ana*" forms. The HOMO and LUMO were calculated by B3LYP/6-311++G(d,p) method. The transition state (TS) structure of photochromism reaction was obtained by using the QST3 method.

# 3. Results and discussion

## 3.1. Geometrical parameters

No X-ray crystallographic data of this molecule has yet been reported. The labeling of atoms in title compound is given in Fig. 1. The optimized structural parameters of title compound calculated at the B3LYP level of theory using 6-311++G(d,p) basis set were listed in Table S4. Some selected geometric parameters (Å, °) of "*trans*" and "*ana*" forms are presented in Table 1. However, the the-

oretical results obtained for "trans" and "ana" forms (Fig. 1) are almost comparable with the reported structural parameters of the parent molecule. The energies of title compound were determined as -1108.6459122 hartree ("trans") and -1108.5989612 hartree ("ana") by B3LYP/6-311++G(d,p) level of theory, so that "trans" form is more stable than "ana" form by 123.150 kJ mol<sup>-1</sup>. X-ray crystal structure of unsubsituted anthraquinone, reported the C=O bond length of the molecule in the crystal to be 1.224 Å [28]. X-ray crystal structures of substituted anthraquinones, showed that the C=O bond length depends on the substitution pattern. Thus, the C=O bond length is 1.223 Å for 1,4-diphenylanthraquinone [29], 1.212 for 1,8-bis(nicotinyl)anthraguinone and 1.205 Å for 1,8-bis(thiazolyl)anthraquinone [30]. B3LYP/6-311G(d) calculations by Krishnakumar and Xavier [31] seem to give exaggerated bond lengths of 1.42 Å and 1.43 Å for the C=O groups in 1.5-dichloroanthraguinone. From the Table 1. the C=O bond length are 1.2185–1.2198 Å "trans" and 1.2216–1.2282 Å for "ana" forms, which are in agreement with the reported values.

Further calculate the average bond length of title compound in "*trans*" form (see Table 1),  $C_4$ — $C_8$  = 1.4955,  $C_3$ — $C_4$  = 1.4037,

Table 2

Comparison of the observed and calculated (scaled) selected frequencies (cm<sup>-1</sup>) and assignments of the fundamental modes for "trans" and "ana" forms.<sup>a</sup>

Modes No.	. "trans" form			"ana" form						
	Theor	etical		Exp.	Assignment	Theor	retica	al	Exp.	Assignment
	Freq.	I.IR	A <sub>R</sub>	FT-IR		Freq.	I.IR	$A_{\rm R}$	FT-IR	
υ <sub>104</sub>	3081	10	167	3080(4)	RI[UCH <sub>s</sub> ]	3095	3	105	3094(2,sh)	RI[UCH <sub>s</sub> ]
υ <sub>100</sub>	3074	2	150	3069(5)	RIII[vCH <sub>as</sub> ]	3074	5	146	3072(3)	RII[vCH <sub>as</sub> ]
U99	3063	10	202	2959(6,sh)	RI[vCH <sub>as</sub> ]	3066	14	257	2960(2)	RI[UCH <sub>as</sub> ]
U97	3057	6	104	2924(19)	RIII[UCH <sub>as</sub> ]	3052	3	90	2925(4)	RI[UCH <sub>as</sub> ]
U <sub>95</sub>	3039	9	94	2801(3)	RII[vCH <sub>as</sub> ]	3043	11	103	2900(1,sh)	RIII[UCH <sub>as</sub> ]
$v_{94}$	2769	144	212	2853(12)	RII[vC <sub>35</sub> —H <sub>37</sub> ]	2763	173	211	2853(1)	RII[vC <sub>35</sub> —H <sub>37</sub> ]
U93	1690	325	217	1680(98)	RII[υC=O, δC <sub>35</sub> -H <sub>37</sub> ]	1708	286	137	1679(95)	RII[υC=O, δC <sub>35</sub> -H <sub>37</sub> ]
υ <sub>90</sub>	1577	236	355	1601(45,sh)	$RII[\delta CH + \upsilon s(C_{15} - O_{24} - C_{25})] + RIII[\upsilon Ph]$	1583	6	7	1599(31,sh)	RII[ $\delta$ (CH), $\upsilon$ (C=O)] + RQ[ $\upsilon$ (C=O)]
$v_{88}$	1559	194	40	1583(75)	RIII[ $\upsilon$ Ph, $\delta$ CH] + RQ[ $\upsilon$ Ph] + RI[ $\upsilon$ Ph]	1577	274	674	1585(65)	RIII[vPh, oCH]
U85	1540	25	13	1502(44)	RIII[υPh, δ CH] + RI[υPh]	1504	58	395	1502(27)	RIII[ $\nu$ Ph, $\delta$ CH] + RQ[ $\nu$ Ph]
υ <sub>83</sub>	1450	1508	5	1463(12,sh)	RII[vPh, oCH]	1466	170	851	1461(7,sh)	RII[ $\upsilon$ Ph, $\delta$ CH] + RQ[ $\upsilon$ (C—C)] + RI[ $\upsilon$ (C—C)]
υ <sub>82</sub>	1428	32	5	1444(34)	RII[vPh, oCH]	1449	4	443	1443(21)	RI[ $\nu$ Ph, $\delta$ CH] + RQ[ $\nu$ Ph]
υ <sub>81</sub>	1421	11	3	1420(5)	RI[ $\delta$ (CH), $\upsilon$ Ph] + RIII[ $\upsilon$ Ph, $\delta$ CH]	1420	73	140	1419(3)	$RQ[\delta(CH), \nu Ph] + RIII[\nu Ph, \delta CH]$
U79	1399	7	6	1385(63)	RII[ $vPh$ , $\delta CH$ , $\delta C_{35}$ — $H_{37}$ ]	1381	13	210	1386(24)	RIII[vPh, oCH]
U78	1363	8	6	1358(13)	RII[ $\delta C_{35}$ —H <sub>37</sub> , $\upsilon Ph$ ]					
U77	1309	1	11	1325(59)	RI[vPh] + RII[vPh]	1347	41	90	1323(50)	RII[vPh, oCH]
U75	1290	134	14	1314(37)	RII[ $\nu$ Ph, $\delta C_{35}$ —H <sub>37</sub> ] + RIII[ $\nu$ Ph]	1294	77	45	1316(25)	RII[ $vPh$ , $\delta C_{35}$ —H <sub>37</sub> ]
U73	1270	106	31	1279(54,sh)	$RI[\delta CH] + RIII[\delta CH] + RQ[\nu Ph]$	1269	183	41	1277(42sh)	$RIII[\delta(CH)] + RQ[\upsilon(C-C)] + RI[\delta(CH)] + RIII[\delta(CH)]$
U72	1243	363	10	1254(82)	$RQ[vPh] + RI[\delta CH] + RIII[va (C_{15}-O_{24}-C_{25})]$	1259	145	117	1255(87)	$RII[\delta CH] + RQ[\upsilon C - O, \upsilon Ph]$
U <sub>71</sub>	1221	659	32	1217(50)	RIII[ $\upsilon a(C_{15}-O_{24}-C_{25}), \delta CC] + RI[\delta CH]$	1200	294	58	1217(35)	$RQ[\upsilon s(C_8 - O_{24} - C_{25})] + RI[\delta CH] + RIII[\upsilon Ph, \delta CH]$
U <sub>69</sub>	1188	123	68	1190(6)	RIII[ $\upsilon s(C_{15}-O_{24}-C_{25}),$	1187	272	190	1191(3)	RIII[ $\upsilon$ Ph] + RI[ $\delta$ CH] + RII[ $\upsilon$ Ph, $\upsilon$ s(C—O—C)]
					$\delta CH$ ] + RI[ $\delta CH$ ] + RII[ $\upsilon Ph$ ]					
U <sub>67</sub>	1161	12	79	1158(51)	$RI[\delta CH] + RQ[\upsilon Ph] + RIII[\delta CH]$	1152	3	52	1154(33)	RI[ $\delta$ CH, $\delta$ CCC] + RQ[ $\upsilon$ Ph] + RIII[ $\delta$ CH, $\upsilon$ Ph]
υ <sub>64</sub>	1130	69	22	1128(3)	$RIII[\delta CH] + RI[\upsilon Ph] + RII[\delta CH]$	1123	57	56	1128(2)	RIII[ $\delta$ CH] + RI[ $\upsilon$ Ph] + RII[ $\delta$ CH]
U <sub>63</sub>	1129	122	107	1103(18)	$RII[\delta CH] + RI[\delta CH] + RIII[\delta CH]$	1106	7	5	1103(10)	$RI[\delta CH] + RQ[\upsilon s(C_8 - O_{24} - C_{25})] + RIII[\delta CH]$
U <sub>62</sub>	1086	6	2	1074(9,sh)	RII[8CH]	1084	8	2	1073(4,sh)	RII[8CH]
υ <sub>60</sub>	1052	0	50	1042(8)	RIII[oCH, vPh]	1039	3	9	1044(4)	$RI[\delta CH] + RIII[\nu Ph, \delta CH]$
U59	1019	1	63	1010(18)	$RI[\delta CH, \nu Ph]$	1015	6	22	1010(10)	$RI[vPh] + RIII[vPh, \delta CH]$
U56	984	21	16	976(5)	RII[ $\delta$ CH, $\upsilon$ Ph] + RIII[ $\upsilon$ C—O] + RO[ $\upsilon$ Ph]	987	4	2	976(2)	RII[8CC]
U53	965	1	0	930(5)	RI[ <sub>Y</sub> CH]	958	1	0	932(2)	RI[ <sub>Y</sub> CH]
U <sub>49</sub>	893	6	13	888(40)	$RI[\delta CC] + RIII[\delta CC] + RO[\nu Ph, \delta CO]$	894	9	9	888(23)	$RI[\delta CC] + RIII[\delta CC] + RQ[\delta CO]$
U <sub>47</sub>	869	115	5	854(19)	RII[ $\delta CC$ , $\upsilon s(C_{15} - O_{24} - C_{25})$ ] + RO[ $\delta CO$ ]	847	37	22	853(10)	$RI[\gamma CH] + RIII[\gamma CH, \delta CC] + RII[\delta CC]$
U <sub>46</sub>	828	48	32	831(40)	$RII[\gamma CH] + RIII[\gamma CH]$	835	22	25	831(23)	$RIII[\gamma(CH)] + RII[\delta(CCC)] + RI[\gamma(CH)]$
U44	810	46	1	804(21)	$RII[\gamma CH] + RIII[\gamma CH]$	811	45	1	804(12)	RII[vCH]
1)20	748	8	2	739(9)	$RI[\gamma CH] + RIII[\gamma CH]$	739	20	2	738(5)	$RI[\gamma CH] + RIII[\gamma CH] + RO[\gamma ring]$
U38	719	25	1	709(42)	$RI[\gamma CH] + RO[\gamma ring] + RIII[\gamma ring]$	694	33	8	709(25)	$RI[\gamma CH] + RO[\gamma ring] + RIII[\gamma ring]$
U35	676	3	1	676(9)	$RI[\delta CC] + RIII[\delta CC] + RO[\delta CO]$	690	12	2	678(4)	$RII[\gamma CH] + RO[\gamma ring] + RI[\gamma CH]$
U32	625	7	7	628(6.sh)	$RII[\delta CC] + RI[\delta CC] + RIII[\delta CC]$	624	2	11	628(3.sh)	RIII[ $\delta$ CC] + RI[ $\gamma$ ring] + RO[ $\gamma$ ring]
- 32 U30	601	13	2	608(7)	RIII[ $\gamma$ ring] + RO[ $\gamma$ ring] + RII[ $\delta$ CO, $\delta$ CC]	567	4	2	604(4)	RII[SCC] + RI[SCC]
- 30 U28	504	12	3	515(15)	$RIII[\gamma ring] + RI[\gamma ring] + RO[\gamma ring]$	530	2	8	515(8)	$RIII[\gamma ring] + RI[\gamma ring] + RO[\gamma ring]$
1)22	441	6	10	448(5)	$RO[\delta ring] + R[[\delta ring] + R[[[\delta ring]]]$	458	5	1	448(4)	$R[[\gamma ring] + R[[[\gamma ring] + RO[\gamma ring]]$
~ 2.3		0		(- )	Sec. 101		5	-	(-)	

<sup>a</sup> Freq., vibrational wavenumber (calculated at the B3LYP/6-311++G(d,p)level); I.IR, IR intensities in km/mol; I.R., Raman scattering activities in A\*\*4/AMU; experimental relative intensities are given in parenthesis; R: ring; sh, shoulder; υ, stretching; δ, in-plane bending; γ, out-of-plane bending; as, asymmetric; s, symmetric.

 $C_4-C_5 = 1.3988$ ,  $C_5-C_6 = 1.3895$ ,  $C_6-C_1 = 1.3982$  Å, and for "ana" form.  $C_4 - C_8 = 1.4607$  $C_3 - C_4 = 1.4105$ ,  $C_4 - C_5 = 1.4044$ ,  $C_5-C_6 = 1.3888$ ,  $C_6-C_1 = 1.3966$  Å are comparable to values, 1.478, 1.372, 1.395, 1.376, 1.410 Å obtained from the X-ray crystal structure of unsubsituted anthraquinone [28]. According to our calculations, at C<sub>8</sub> of "trans" form, the exocyclic angle  $C_{14}$ - $C_{15}$ - $O_{24}$ is reduced by  $3.8^{\circ}$  and  $C_9-C_{15}-O_{24}$  is increased by  $2.6^{\circ}$  from  $120^{\circ}$ , which shows the interaction between  $H_{21}$  and  $O_{24}$ . At  $C_8$ , there is also an interaction between  $H_{18}$  and  $O_{22}$ . For "ana" form, the exocyclic angle  $C_4 \!\!-\!\! C_8 \!\!-\!\! O_{24}$  is reduced by 6.7° and  $C_9 \!\!-\!\! C_8 \!\!-\!\! O_{24}$  is increased by 4.0° from 120°, which shows the interaction between  $H_{18}$  and  $O_{24}.$  This departure of the exocyclic angles from  $120^\circ$  can be found in the crystal structures of the anthraquinones [28]. As calculated torsion angles shown, the anthraquinone core is not planar, so that for "trans" form  $C_6-C_5-C_4-C_8 = -179.5$ ,  $C_5-C_4-C_{8-1}$  $\begin{array}{l} \text{Har, 55 that for mass form } c_{5}^{-} c_{5}^{-} c_{4}^{-} c_{8}^{-} - 179.8, \ c_{5}^{-} c_{4}^{-} c_{8}^{-} - 179.8, \ c_{2}^{-} - c_{3}^{-} - c_{4}^{-} - c_{8}^{-} - 0_{23}^{-} = -177.8, \ c_{2}^{-} - c_{3}^{-} - c_{7}^{-} - 0_{23}^{-} = 179.0, \ c_{14}^{-} - c_{15}^{-} - c_{9}^{-} - c_{8}^{-} - 177.8, \ c_{15}^{-} - c_{9}^{-} - c_{8}^{-} - 177.8, \ c_{15}^{-} - c_{9}^{-} - c_{8}^{-} - c_{4}^{-} - 177.2, \ c_{11}^{-} - c_{10}^{-} - c_{7}^{-} - c_{23}^{-} = 2.3 \ \text{ and } \ c_{2}^{-} - c_{3}^{-} - c_{7}^{-} - c_{10}^{-} = 178.6^{\circ}. \ \text{Same as} \end{array}$ "trans" form, these explanations are valid for "ana" form. Again, from the X-ray crystal structure of anthraquinones, especially for hindered aryl anthraquinones, shows a significant distortion of the anthraquinone core [32].

#### 3.2. Vibrational analysis

The title compound that consists of 37 atoms and 105 normal modes has been assigned according to the detailed motion of the individual atoms. There is no detailed quantum chemical study for the vibrational spectra of title compound in literature. The observed IR bands, calculated wavenumbers (scaled) and assignments were given in Tables 2 and plotted in Fig. 2. Deconvoluted IR spectra of "*trans*" and "*ana*" forms were depicted in Supplementary data (Fig. S1). At this level of theory, the calculated harmonic force constants and frequencies are higher than the experimental values, due to basis set truncation and neglecting of electron correlation as well as mechanical anharmonicity [33]. To compensate these shortcomings, scale factors were introduced and a description of this approach was explained [34,35].

It can be seen from Fig. S2 (which shows the theoretical FT-IR spectra along with the experimental spectra for "*trans*" and "*ana*" forms) there is an excellent correlation between the theoretical and experimental FT-IR spectra. As can be seen from Fig. S2, experimental fundamentals have a good correlation with B3LYP. The relations between the calculated and experimental wavenumbers are linear and described by the following equations:

For "trans" form  $v_{cal.} = 0.9709v_{cal.} + 28.932$  ( $R^2 = 0.9965$ )

For "ana" form 
$$v_{cal} = 0.9775v_{cal} + 22.969$$
 ( $R^2 = 0.9978$ )

As a result, the scaled fundamental vibrational are in good consistency with the experimental results and are found a good agreement above the predicated literature.

#### 3.2.1. C-O and C=O vibrations

Infrared active C=O stretching vibrations for anthraquinones have been reported in the region 1630–1680 cm<sup>-1</sup>, with unsubstituted anthraquinone at 1676 cm<sup>-1</sup> [36], 2-methylanthraquinone at 1672 cm<sup>-1</sup> [37], 1,4-dimethylanthraquinone at 1668 cm<sup>-1</sup> [37], and 2-hydroxy-methylanthraquinone at 1679 cm<sup>-1</sup> [36].

According to our deconvolution results, the IR spectrum of "*trans*" form indicate the presence of one band for C=O stretching vibrations at 1680 cm<sup>-1</sup> (Fig. S1a) and 1690 cm<sup>-1</sup> (B3LYP). It shows the presence of two bands at 1679 and 1599 cm<sup>-1</sup> for "*ana*" form



Fig. 2. FT-IR spectra (experimental) for "*trans*" quinone, before irradiation; and "*ana*" quinone, after irradiation by 300 nm wavelength.

Table 3

Second-order perturbation theory analysis of Fock matrix in NBO basis corresponding to the intramolecular bonds of "trans" and "ana" forms (donor  $\rightarrow$  acceptor).<sup>a</sup>

Donor (i)	Туре	Acceptor (j)	Туре	" <i>trans</i> " form $E^{(2)b}$	"ana" form $E^{(2)b}$
$C_1 - C_2$	π	$C_3 - C_4$	$\pi^*$	45.78	47.15
		$C_5 - C_6$	$\pi^{*}$	44.20	44.19
$C_3 - C_4$	π	$C_1 - C_2$	$\pi^{*}$	42.71	42.65
		$C_5 - C_6$	$\pi^*$	42.50	41.57
		C <sub>7</sub> —0	$\pi^*$	19.03	19.05
		C <sub>8</sub> —0	$\pi^{*}$	17.67	23.01
$C_5 - C_6$	π	$C_1 - C_2$	$\pi^{*}$	44.05	43.88
		$C_3 - C_4$	$\pi^*$	46.17	43.61
C7-0	π	$C_3 - C_4$	$\pi^*$	8.95	9.11
C <sub>8</sub> —O	π	$C_3 - C_4$	$\pi^*$	8.85	1.33
		$C_9 - C_{10}$	$\pi^*$	8.56	1.39
$C_9 - C_{10}$	π	C7-0	$\pi^*$	16.78	21.80
		C <sub>8</sub> —0	$\pi^*$	18.70	23.35
		C <sub>11</sub> -C <sub>13</sub>	$\pi^*$	41.65	23.51
		C <sub>14</sub> -C <sub>15</sub>	$\pi^*$	46.02	25.71
$C_9 - C_{15}$	σ	$C_{15} - O_{24}$	$\sigma^{*}$	3.27	2.22
C <sub>11</sub> -C <sub>13</sub>	π	C <sub>9</sub> -C <sub>10</sub>	$\pi^*$	50.16	24.62
		C <sub>14</sub> -C <sub>15</sub>	$\pi^*$	46.99	23.89
$C_{14} - C_{15}$	π	C <sub>9</sub> -C <sub>10</sub>	$\pi^*$	42.25	23.89
		C <sub>11</sub> -C <sub>13</sub>	$\pi^*$	45.37	24.62
$0_{24} - C_{25}$	σ	C <sub>14</sub> -C <sub>15</sub>	$\pi^*$	5.16	-
$C_{25} - C_{27}$	π	$C_{26} - C_{28}$	$\pi^*$	36.55	37.65
		$C_{30} - C_{32}$	$\pi^*$	55.95	54.25
$C_{26} - C_{28}$	π	$C_{25} - C_{27}$	$\pi^*$	49.70	50.35
		$C_{30} - C_{32}$	$\pi^*$	36.31	37.92
$C_{30} - C_{32}$	π	$C_{25} - C_{27}$	$\pi^*$	40.85	42.53
		C <sub>26</sub> -C <sub>28</sub>	$\pi^*$	50.78	50.18
		$C_{35} - O_{36}$	$\pi^{*}$	22.08	21.31
LP(2) O <sub>22</sub>	n	$C_4 - C_8$	$\pi^{*}$	29.15	29.30
		$C_8 - C_9$	$\pi^*$	29.98	29.53
LP(2) O <sub>23</sub>	n	$C_3 - C_7$	$\pi^*$	28.64	29.85
		$C_7 - C_{10}$	$\pi^*$	29.69	27.15
$LP(1) O_{24}$	n	$C_{14} - C_{15}$	$\pi^*$	8.24	-
		$C_8 - C_9$	$\pi^*$	-	6.56
LP(2) O <sub>24</sub>	n	C <sub>9</sub> -C <sub>15</sub>	$\sigma^*$	10.68	-
		$C_8 - C_9$	$\sigma^*$	-	6.75
		$C_{14} - C_{15}$	$\sigma^*$	9.23	-
		C <sub>9</sub> -C <sub>10</sub>	$\pi^*$	-	18.89
		C <sub>25</sub> -C <sub>27</sub>	$\pi^*$	41.31	29.28
LP(2) O <sub>36</sub>	n	$C_{32} - C_{35}$	$\sigma^*$	29.73	30.26
		C <sub>35</sub> —H <sub>37</sub>	$\sigma^*$	31.52	31.86

<sup>a</sup> Energy in kcal/mol.

<sup>b</sup>  $E^{(2)}$  means energy of hyper-conjugative interactions (stabilization energy).



Fig. 3. Atomic charge distribution of "trans" and "ana" forms.

(see Fig. S1b). Wavenumbers 1709 and 1583  $\text{cm}^{-1}$  (B3LYP) were assigned the C=O stretching vibrations.

#### 3.2.2. Ring vibrations

Since the identification of all the normal modes of vibrations belong to large molecules is not trivial, we tried to simplify the problem by considering each molecule as substituted benzene. Such an idea has already been successfully utilized by several authors for the vibrational assignments of molecules containing multiple homo and hetero-aromatic rings [38,39]. In the following discussion, the benzoannelation of the quinone system Oring were designated as RI, and RIII, respectively, that RI-Oring-RIII representing the anthraquinone core. The para substituted phenyl ring is designated as RII. The modes in the benzaldehyde rings and the phenyl substituent will differ in wavenumber, and the magnitude of splitting will depend on the strength of interaction between different parts (internal coordinates) of the rings. For some modes, this splitting is so small that they may be considered as quasi-degenerate and for other modes a significant amount of splitting is observed [38,39]. The benzene ring possesses six ring stretching vibrations, of which the four with the highest wavenumbers (occurring respectively near 1600, 1580, 1490 and 1440  $\text{cm}^{-1}$ ) are good group vibrations [40]. The bands for the phenyl ring of "ana" form,  $\upsilon$ Ph, were observed in the range of 976–1583 cm<sup>-1</sup> (in the IR spectrum),  $984-1559 \text{ cm}^{-1}$  (in DFT) and for "ana" form were observed at  $1010-1585 \text{ cm}^{-1}$  (in the IR spectrum), 1015-1577 cm<sup>-1</sup> (in DFT). Some phenyl ring stretching modes,  $\upsilon$  Ph ring, are not pure, but also contain significant contributions from other modes. The ring breathing mode for para-disubstituted benzenes with entirely different substituents are expected to be strongly IR active with typical bands in the interval of  $780-840 \text{ cm}^{-1}$  [41]. For the "trans" and "ana" forms, this band was confirmed by the strong band in the IR spectrum at 831 cm<sup>-1</sup> which are the same as computational results. Ambujakshan et al. [42] reported a value 792 cm<sup>-1</sup> (IR) and 782 cm<sup>-1</sup> (calculated) as ring breathing mode of para substituted benzenes. In overall comparison, Baran et al. [43] reported υQring at 1273, 1143, 1090, 1044, 1027 cm<sup>-1</sup>, δQring at 1292, 823 cm<sup>-1</sup> in the Raman spectrum of the silver surface complexed anthraquinone alizarin.

#### 3.2.3. C—H vibrations

The aromatic C—H stretching vibrations are normally found between 3100 and 2900 cm<sup>-1</sup>. In this region the bands are not affected appreciably by the nature of substituents. In "*trans*" form the bands observed at 2801, 2924, 3959, 3069 and 3080 cm<sup>-1</sup> in the IR spectrum are assigned as the C—H stretching modes of the phenyl rings. The B3LYP calculations give these modes in the range 3039–3081 cm<sup>-1</sup>. For "*ana*" form, the bands observed at 2900, 2925, 2560, 3072 and 3094  $\text{cm}^{-1}$  in the IR spectrum are assigned as the C—H stretching modes of the phenyl rings. The B3LYP calculations give these modes in the range of 3043-3095 cm<sup>-1</sup>. The band observed for "trans" form at 2853 cm<sup>-1</sup> in the IR spectrum, 2763 cm<sup>-1</sup> (DFT) and for "ana" form at 2853 cm<sup>-1</sup> in the IR spectrum, 2763 cm<sup>-1</sup> (DFT) were assigned as C<sub>35</sub>—H<sub>37</sub> stretching mode. According to Roeges [40], in the case of ortho-substitution, only one strong absorption in the region of  $755 \pm 35$  cm<sup>-1</sup> is observed that is due to the out-of-plane  $\gamma$ CH mode. This was confirmed by the presence of a strong band for "trans" and "ana" forms at 709 and 709 cm<sup>-1</sup> in the IR spectrum and was supported by the calculated result at 719 and 694 cm<sup>-1</sup>. Two very strong  $\gamma$ CH deformation bands, occurring at  $840 \pm 50 \text{ cm}^{-1}$ , are typical for 1,4-di-substituted benzenes [40]. A very strong  $\gamma$ CH was observed at 831 cm<sup>-1</sup> for "ana" and "trans" forms in the IR spectrum. Again according to the literature [44,45] a low  $\gamma$ CH absorption can be found in the neighborhood, at  $820 \pm 45$  cm<sup>-1</sup>, but it is much weaker or infrared inactive. The DFT calculations gave a  $\gamma$ CH at 825 and 813 cm<sup>-1</sup> for "trans" and "ana" forms, respectively and no band was experimentally observed for this mode. The aromatic C-H in-plane bending modes of benzene and its derivatives are observed in the region of  $1300-1000 \text{ cm}^{-1}$ .

## 3.3. NBO analysis

The natural bond orbitals (NBOs) calculations were performed using NBO 3.1 program [46] as implemented in the Gaussian03 package at the DFT (B3LYP)/6-311++G(d,p) level to understand various second-order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbital and formally unoccupied (anti-bond or Rydberg) non-Lewis NBO orbital correspond to a stabilizing donoracceptor interaction. Some electron donor, acceptor orbitals and the interacting stabilization energy resulting from the second-order micro-disturbance theory were reported [47].

The second-order Fock-matrix was calculated to evaluate the donor–acceptor interactions in the NBO basis [48]. The interactions result in a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (*i*) and acceptor (*j*) the stabilization energy  $E^{(2)}$  associated with the delocalization  $i \rightarrow j$  is determined as

$$E^{(2)} = \Delta E_{ij} = q_i \frac{(F_{ij})^2}{(E_j - E_i)^2}$$
(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. In NBO analysis, large  $E^{(2)}$  value shows the intensive interaction between



Fig. 4. (a) <sup>1</sup>H NMR (400.224 MHz, CDCl<sub>3</sub>) spectrum of "trans" form at 294.8 K. (b) Expanded <sup>1</sup>H NMR spectrum in the region of 7.0–8.4 ppm.

electron-donors and electron-acceptors, and greater the extent of conjugation of the whole system. The possible intensive interactions were given in Table 3. The second-order perturbation theory analysis of Fock-matrix in NBO basis shows strong intermolecular hyper-conjugative interactions formed by orbital overlap between n(O) and  $\sigma^*(C-H)$ ,  $\sigma^*(C-C)$ ,  $\pi^*(C-C)$  bond orbitals which result in ICT causing stabilization of the system. These interactions are observed as an increase in electron density (ED) in C-C and C-H anti bonding orbital that weakens the respective bonds.

There occurs a strong intra-molecular hyper-conjugative interaction on "*trans*" form in  $C_{25}-C_{27}$  from  $O_{24}$  of  $n2(O_{24}) \rightarrow \pi^*$ ( $C_{25}-C_{27}$ ) which increases ED (0.38 e) that weakens the respective bonds leading to stabilization of 41.31 kcal mol<sup>-1</sup> and also the hyper-conjugative interaction in  $O_{36}$  of  $n2(O_{36})\rightarrow\sigma^*(C_{35}-H_{37})$  which increases ED (0.05 e) that weakens the respective bonds  $C_{35}$ – $H_{37}$  leading to stabilization of 31.52 kcal mol<sup>-1</sup>. The increased electron density at the oxygen atoms leads to the elongation of respective bond length and a lowering of the corresponding stretching wave number. The intra-molecular interaction is formed by the orbital overlap between  $\pi$  (C–C) and  $\pi^*$ (C–C) bond orbital which results intra-molecular charge transfer (ICT) causing stabilization of the system. These interactions are observed as increase in electron density (ED) in C–C antibonding orbital that weakens the respective bonds [49]. The electron density of six conjugated single bond of aromatic ring (~1.9 e) clearly demonstrates strong delocalization. NBO analysis clearly manifests the evidences of the intra-molecular charge transfer from  $\pi$  ( $C_{25}$ – $C_{27}$ ) to  $\pi^*$ ( $C_{26}$ – $C_{28}$ ) and  $\pi^*$  ( $C_{30}$ – $C_{32}$ ) antibonding orbital's as shown in Table 2 which



Fig. 5. <sup>13</sup>C NMR spectrum of "trans" form in CDCl<sub>3</sub>.

increases ED (0.32 and 0.36 e) that weakens the respective bonds leading to stabilization of 36.55 and 55.95 kcal mol<sup>-1</sup>. These comments also apply for "*ana*" form.

#### 3.4. Charge distribution

The calculation of atomic charges plays an important role in the application of quantum mechanical calculations to molecular systems [50]. The charge distributions over the atoms suggest the formation of donor and acceptor pairs involving the charge transfer in the molecule. The calculated natural charges of "trans" and "ana" forms by B3LYP/6-311++G(d,p) method are shown in Fig. 3. The charge distribution of "trans" and "ana" forms shows that the carbon atom attached to hydrogen atoms is negative, whereas the remaining carbon atoms are positively charged. The oxygen atoms have more negative charges whereas all the hydrogen atoms have positive charges. Negatively charged lone pair oxygen atoms shows that charge is transferred from 0 to H ( $O_{22} \rightarrow H_{18}, O_{23} \rightarrow H_{17}, H_{12}$ and  $O_{24} \rightarrow H_{21}$ ) for "trans" form and  $(O_{24} \rightarrow H_{18}, O_{23} \rightarrow H_{17}, H_{12})$ and  $O_{22} \rightarrow H_{21}$ ) for "ana" form. The positive charges on the carbon and hydrogen atoms C<sub>7</sub>, C<sub>8</sub>, C<sub>15</sub>, C<sub>25</sub>, C<sub>35</sub>, H<sub>18</sub>, H<sub>17</sub>, H<sub>12</sub> and H<sub>21</sub> become more positive. Restructuring from the "trans" form into "ana" form reduces the charge on  $C_{15}(0.21751 \rightarrow 0.18909 \text{ e})$ ;  $O_{24}(-0.25977 \rightarrow -0.22394 \text{ e})$ , against increase charge on  $C_8(0.23326 \rightarrow 0.25846 \text{ e}); \ O_{22}(-0.2306 \rightarrow -0.25605 \text{ e}).$ 

# 3.5. NMR spectral studies

Full geometry optimization of "*trans*" and "*ana*" forms was performed at DFT (B3LYP)/cc-pVTZ method. Then, Gauge-Independent Atomic Orbital (GIAO) chemical shift calculations of the title compound have been made by same method [51]. The experimental NMR data for "*trans*" form in CDCl<sub>3</sub> with TMS as internal standard was obtained at 400 MHz and listed in Table S5. It could be seen that chemical shift was in agreement with the experimental NMR data.

The observed <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the compound "*trans*" form were given in Figs. 4 and 5, respectively. Aromatic carbons give signals in overlapped areas of the spectrum with

chemical shift values from 100 to 200 ppm [52]. In the present work, <sup>13</sup>C NMR chemical shifts in the ring for the title molecule are >100 ppm, as they would be expected (in Table S5). Oxygen atoms show electronegative property. Therefore, the chemical shift value of  $C_{15}$ ,  $C_{25}$ ,  $C_8$ ,  $C_7$  and  $C_{35}$  in the ring calculated by B3LYP/ccpVTZ level, were 161.826, 174.041, 188.797, 190.424 and 197.398 ppm, respectively. Experimental C—O chemical shifts (with respect to TMS) are 154.27, 162.90, 181.42, 182.53 and 190.74 ppm. The protons are located on the periphery of the molecular solute–solvent effects than the carbon atoms and usually the agreement between the experimental and calculated shifts for <sup>1</sup>H is slightly deviated from <sup>13</sup>C [53].

#### 3.6. 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 "*trans*" and "*ana*" forms using density functional B3LYP level with 6-311++G(d,p) basis set. 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 [54]. The electrostatic potential V(r) is also well suited for analyzing processes based on the "recognition" of one molecule by another, because it is through their potentials that the two species first "see" each other [55,56].

The negative  $(red^1)$  regions of MEP were related to electrophilic reactivity and the positive (blue) regions to nucleophilic reactivity (Fig. 6). Fig. 6 shows the computationally observed MEP surface map with the fitting point charges to the electrostatic potential V(r) for title compound. The different values of the electrostatic potential at the surface are represented by different colors. Potential increases in the order red < orange < yellow < green < blue. The predominance of the light green region in the MEP surface corresponds to a potential halfway between the two extreme regions

 $<sup>^{1}\,</sup>$  For interpretation of color in Fig. 6, the reader is referred to the web version of this article.





**Fig. 6.** Molecular electrostatic potential surface (left) and the point charges, electric potential values (right) on atom for "*trans*" and "*ana*" forms calculated by B3LYP/6-311++G(d,p) level. (For interpretation of the references to color in this figure, the reader is referred to the web version of the article.)

red and dark blue color. These sites give information about the region where the compound can have intermolecular interaction. A negative electrostatic potential region is observed around the O<sub>22</sub>, O<sub>23</sub>, O<sub>24</sub> and O<sub>36</sub> atoms. The average maximum negative electrostatic potential value for these electrophilic sites calculated at B3LYP/6-311++G(d,p) are about -22.36 a.u. Also a maximum positive region is localized on the hydrogen atoms indicating a possible site for nucleophilic attack. The MEP map shows that the negative potential sites are on electronegative atoms as well as the positive potential sites are around the hydrogen atoms. The MEP provides a visual representation of the chemically active sites and comparative reactivity of the atoms.

# 3.7. HOMO-LUMO band gap

The energy gap between HOMO and LUMO is a critical parameter in determining molecular electrical transport properties [57]. The conjugated molecules are characterized by a highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) separation, which is the result of a significant degree of ICT from the end-capping electron-donor groups to the efficient electron-acceptor groups through  $\pi$ -conjugated path. Therefore, an ED transfer occurs from the more aromatic part of the  $\pi$ -conjugated system in the electron-donor side to its electron-withdrawing part. HOMO and HOMO - 1 and second highest and lowest unoccupied molecular orbitals LUMO and LUMO + 1 were shown for title compound and transition state in Figs. 7 and S3. The HOMO shows that the charge density localized mainly on carbonyl group whereas LUMO is localized on ring system. The energy of HOMO is directly related to the ionization potential and the energy of LUMO is related to the electron affinity. The energy gap of HOMO-LUMO explains the eventual charge transfer interaction within the molecule, and the frontier orbital gap in case of "trans" and "ana" forms is found to be 3.4051 eV and 2.7412 eV obtained at TD-DFT method using 6-311++G(d,p) basis set. Moreover, lower values in the HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule.

#### 3.8. UV-Vis spectra analysis

All the molecular structure allows strong  $\pi$ - $\pi$ \* transition in the UV-vis region with a high extinction coefficient. The lowest singlet  $\rightarrow$  singlet spin-allowed excited states were taken into account to investigate the properties of electronic absorption. On the basis of a fully optimized ground state structure, the electronic spectra of title compound were computed in the dichloromethane environment using TD-DFT method [58] and PCM model [59] employing B3LYP/6-311++G(d,p) functional (Table 4). Experimentally observed UV-vis absorption spectrum of "*trans*" and "*ana*" molecules recorded in CH<sub>2</sub>Cl<sub>2</sub> solvent is presented in Fig. 8. In an attempt to understand the nature of electronic transitions, positions of experimental absorption peaks, calculated absorption peaks ( $\lambda_{max's}$ ),

oscillator strengths (f) and assignments of the transitions of the title compound molecule were calculated and the results presented in Table 4. Common types of electronic transitions in organic compounds are  $\pi - \pi^*$ ,  $n - \pi^*$  and  $\pi^*$ (acceptor)- $\pi$ (donor). The strong bands in "trans" form were observed experimentally at 330 and 270 nm and calculated at 332.74 and 273.88 nm in the solvent dichloromethane. For "ana" form the bands observed at 475, 330 and 270 nm (experimental values). Observed band at 270 nm is due to the  $n-\pi^*$ . The strong absorption peak observed at 330 nm is caused by the  $\pi \rightarrow \pi^*$  transition. The more intense band observed at 475 nm for "ana" form belonged to the dipole-allowed  $\pi$ - $\pi$ \* transition. The broadening and intensity enhancement of the UV-Vis absorption spectrum clearly indicates the charge transfer interaction. "ana" form was also converted to "trans" form either by stirring in the dark for two days or after being held at 90 °C for 4-5 min.

Certainly the density based methods are useful descriptor for the excited state nature, but the orbital based ones, such as NTO,



39





are also required when inspecting the excitation spectra in detail (e.g., transition moment). The analysis reveals a pair of orbitals, one occupied and one unoccupied, that correspond to a rough electron and hole picture of the electronic excitation (Fig. S3). It is clear that the former is localized on total molecule while the latter is delocalized over anthraquinone part. The NTOs in these figures can also give a clear interpretation on the oscillator strengths of the corresponding excited states; not only the parity, but also the sufficient spatial overlap between the hole and the electron orbitals is required to form large dipole moment, i.e., oscillator strength. Thus, the combinations of the orbital-based method (NTO) and the density-based one (TD) together with the numerical results would give us clear and precise interpretation of the CT excited state properties of molecules.

## 3.9. Electrochemical properties

The calculations based upon Density functional theory (DFT) (B3LYP; 6-311++G(d,p)) were carried out to obtain information

about the HOMO and LUMO distributions of the title compound. Due to the presence of the electron-rich and an increase in the conjugation lengths, for these forms in Table 5 possess a high HOMO energy level (-6.80 and -6.47 eV) (Fig. 7a and b) [61]. The low LUMO energy of these forms (-3.78 and -3.73 eV) is supposed to facilitate the acceptance of electrons from the cathode.

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) is the energy difference between neutral molecules and the corresponding cationic systems. The electron affinities (EA) is defined as the first unoccupied energy level that injected electrons coming from a vacuum into 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 [62]. IP, EA, reorganization energy ( $\lambda$ ), hole-extraction potential (HEP), and electron-extraction potential (EEP) for "*trans*" and "*ana*" forms listed in Table 5. The charge-transfer rate (k) can be expressed by the following

A. Kanaani et al./Journal of Molecular Structure 1063 (2014) 30-44

Experimental	and calculated absorpt	tion wavelength, energies and osc	cillator strengths of "tr	ans" and "ana" fo	orms using the TD-DFT method a	t the B3LYP/6-3	11++G(d,p) method.
Comp.	Excitation	CI expansion coefficient	λ (Cal.; nm)	<i>E</i> (eV)	Oscillator strength (f)	Expt.	Assignment
trans	Excited state 1						
	<b>80</b> → <b>86</b>	0.41241	332.74	3.7262	0.0787	330	$\pi \to \pi^*$
	<b>81</b> → <b>86</b>	0.38458					
	<b>83</b> → <b>86</b>	0.10466					
	Excited state 2						
	<b>77</b> → <b>86</b>	-0.16106	273.88	4.5270	0.2226	270	$n  ightarrow \pi^*$
	$84 \rightarrow 87$	0.66157					
	84  ightarrow 88	0.16222					
ana	Excited state 1						
	$84 \rightarrow 86$	-0.19615	495.15	2.5040	0.2241	475	$\pi  ightarrow \pi^{*}$
	<b>85</b> → <b>86</b>	0.67697					
	Excited state 2						
	<b>79</b> → <b>86</b>	0.59997	361.04	3.4340	0.0475	330	$\pi  ightarrow \pi^*$
	<b>80</b> → <b>86</b>	-0.22199					
	<b>85</b> → <b>87</b>	-0.14959					
	Excited state 3						
	<b>77</b> → <b>86</b>	0.47619	279.67	4.4332	0.2206	270	$n \rightarrow \pi^*$
	<b>83</b> → <b>87</b>	0.32483					
	<b>84</b> → <b>87</b>	-0.36759					



**Fig. 8.** UV–Vis absorption spectra and oscillator strengths of studied compound upon irradiation under 300 nm light in  $CH_2Cl_2$  before and after successive UV irradiation.

$$k = A \exp\left(-\frac{\lambda}{4Tk_b}\right)$$

where *A* is a constant under certain conditions,  $k_{\rm b}$ , is the Boltzmann constant, and *T* is the temperature. Obviously, lower reorganization energy is necessary to achieve a high charge-transfer rate. *ana* has an IP of 6.43 eV, which is smaller than that of *trans* (6.73 eV), indicating that the hole-transporting ability of *ana* better than that of *trans*. On the other hand, the electron-transporting ability of *ana* 

#### Table 5

Table 4

Calculated  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ , IP, EA, HEP, and  $\lambda$  for trans and ana forms.

an EA of 3.58 eV should be better than that of *trans* with an EA of 3.54 eV. In addition, the  $\lambda_{\text{electron}}$  of *trans* smaller than the corresponding  $\lambda_{\text{hole}}$ , suggesting that the electron-transfer rate is better than the hole-transfer rate.

Cyclic voltammogram of supporting electrolyte is also shown in Fig. 9. Upon scanning the potential from -1.5 to +1.5 V, a reversible oxidation wave was observed at half-wave potential of -0.814 V vs SCE. The oxidation and reduction peaks associated with the HOMO and LUMO levels, respectively. In the part of the paper which deals with experimental results one should discuss EA and IP values rather than HOMO and LUMO levels since the molecular orbitals energies are not observables but originate from quantum chemical approximations. Using cyclic voltammetry the IP was estimated from the onset of the first oxidation peak whereas EA from the onset of the first reduction peak. We have assumed that the energy of the optical gap correctly approximates the energy difference between EA and IP. It is generally indicative of a HOMO/LUMO absorption transition to bear a significant charge-transfer character. The higher HOMO/LUMO energy levels 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. Moreover, the electrochemistry is complicated owing to the reversibility of one of the redox process and the accuracy of the Eg value is relatively limited [64].

# 3.10. Non-linear optical properties

Based on the finite-field approach, the non-linear optical parameters such as dipole moment, polarizability, anisotropy polarizability and first order hyperpolarizability of "*trans*" and "*ana*" molecules were calculated using B3LYP level with

Comp	$E_{\rm HOMO}/E_{\rm LUMO}~(\rm eV)^{\rm a}$	IP	HEP	$\lambda_{hole}^{b}$	EA	EEP	$\lambda_{electron}^{c}$	IP/EA	$E^{\mathrm{ox}}$ onset <sup>d</sup> (V)	Eg <sup>e</sup> (eV)	$E_{\rm HOMO}/E_{\rm LUMO}^{\rm f}~(\rm eV)$
trans ana	-6.80/-3.78 -6.47/-3.73	6.73 6.43	6.17 5.91	0.56 0.52	3.54 3.58	3.87 3.89	0.33 0.31	6.73/3.54 6.43/3.56	-0.87	1.21	-5.27/-4.06

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

<sup>b</sup>  $\lambda_{\text{hole}} = \text{IP} - \text{HEP}.$ 

 $^{\rm C}$   $\lambda_{\rm electron} = {\rm EEP} - {\rm EA}.$ 

<sup>d</sup> Oxidation potential in  $CH_2Cl_2(2 \times 10^{-3} \text{ mol } L^{-1})$  containing 0.1 mol  $L^{-1}$  Bu4NBF4 with a scan rate of 100 mV s<sup>-1</sup>.

<sup>e</sup> Optical energy gaps calculated from the edge of the electronic absorption band.

<sup>f</sup>  $E_{HOMO}$  was calculated by  $E^{ox}$  + 4.4 V, and  $E_{LUMO} = E_{HOMO} - Eg$  [60].

6-311++G(d,p) basis sets. The numerical values of above mentioned parameters were listed in Table S6. Nonlinear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wavenumber, phase, or other physical properties [64]. The first hyperpolarizability ( $\beta_0$ ) of this novel molecular system was calculated using B3LYP/6-311G++(d,p) method, based on the finite field approach. 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 10 components due to the Kleinman symmetry [65]. 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

$$E = E_0 - \sum_{j} \mu_i F_j - \frac{1}{2} \sum_{ij} \alpha_{ij} F_i F_j - \frac{1}{6} \sum_{ij} \beta_{ijk} F_i F_j F_k - \frac{1}{24} \sum_{ijkl} \gamma_{ijkl} F_i F_j F_k F_l + \dots$$
(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)

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

$$(6)$$

It is well known that the higher values of dipole moment, molecular polarizability, and hyperpolarizability are important for more active NLO properties. The calculated dipole moment is equal to 3.98 and 3.74 Debye (D) in "*trans*" and "*ana*" forms. The calculated non-zero and zero values of polarizability  $\alpha_{ij}$  are determined by the diagonal components. Total polarizability ( $\alpha_{tot}$ ) calculated as  $-21.44 \times 10^{-24}$  and  $-21.24 \times 10^{-24}$  esu for two forms of title molecule. The first hyperpolarizability values ( $\langle \beta \rangle$ ) are equal to  $18.871 \times 10^{-31}$  and

 $15.002 \times 10^{-31}$  esu for "*trans*" and "*ana*" forms which comparable with the reported values of similar derivatives [66]. Theoretically, the first hyperpolarizability for "*trans*" and "*ana*" forms respectively are 11.54 and 14.52 times greater than the standard NLO material urea ( $0.13 \times 10^{-30}$  esu) [67].

#### 3.11. Thermodynamic functions

On the basis of vibrational calculation at B3LYP/6-311++G(d,p) a level of theory, the standard statistical thermodynamic functions: heat capacity  $(C_{p,m}^0)$ , entropy  $(S_m^0)$ , enthalpy  $(H_m^0)$  and molecular energy (*E*) for the title compound were obtained from the theoretically calculated frequencies were listed in Table 6. It can be observed that these thermodynamic functions are increasing with temperature ranging from 100 to 800 K due to the fact that the molecular vibrational intensities increase with temperature [68]. The corresponding quadratic equations obtained by B3LYP/6-311++G(d,p) are as follows and the related figure was shown in Supplementary data (Fig. S4).

For "trans" form

$$C_{p,m}^{0} = 0.158 + 0.304T - 1 \times 10^{-4}T^{2} \quad (R^{2} = 0.9992) \\
 S_{m}^{0} = 63.815 + 0.299T - 6 \times 10^{-5}T^{2} \quad (R^{2} = 0.9998) \\
 H_{m}^{0} = -3.233 + 0.096T - 2 \times 10^{-4}T^{2} \quad (R^{2} = 0.9999) \\
 E = 168.850 + 0.020T - 9 \times 10^{-5}T^{2} \quad (R^{2} = 0.9997)
 \right\}$$
(7)

For "ana" form

$$\begin{cases}
C_{p,m}^{0} = 1.175 + 0.306T - 1 \times 10^{-4}T^{2} & (R^{2} = 0.9986) \\
S_{m}^{0} = 64.610 + 0.297T - 6 \times 10^{-5}T^{2} & (R^{2} = 1.0000) \\
H_{m}^{0} = -3.129 + 0.096T - 2 \times 10^{-4}T^{2} & (R^{2} = 0.9999) \\
E = 169.29 + 0.0191T - 9 \times 10^{-5}T^{2} & (R^{2} = 0.9996)
\end{cases}$$
(8)

All the thermodynamic data supply useful information for the further study on the "*trans*" and "*ana*" forms. They can be used to compute the other thermodynamic energies according to relationship of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamics in thermo chemical field.

According to the data in Table S7 the molecular energies of the "*trans*" and "*ana*" forms are very close to each other. So the "*trans*" and "*ana*" forms are practically of equivalent stability, this is reflected in the lowest equilibrium constant values of its reaction.

The values of some thermodynamic parameters (such as zeropoint vibrational energy (ZPVE), thermal energy, specific heat capacity, rotational constants, rotational temperature and entropy) of "*trans*" and "*ana*" forms are listed in Table S7. Scale factors have been recommended [69] for an accurate determining of the ZPVE, thermal energy, specific heat capacity, rotational constants, rotational temperature and entropy.

Table 6

Thermodynamic properties at different temperatures at	B3LYP/6-311++G(d,p) leve	el of theory for "trans"	' and "ana"	forms.
---	--------------------------	--------------------------	-------------	--------

T (K)	$C_{p,m}^0$ (cal/mol K)		S <sup>0</sup> <sub>m</sub> (cal/mol K	()	$H_m^0$ (kcal/mol	)	E (kcal/mol)	
	"trans"	"ana"	"trans"	"ana"	"trans"	"ana"	"trans"	"ana"
100	30.63	30.98	93.83	93.32	9.38	9.33	172.69	172.31
200	51.41	53.89	121.89	121.68	24.38	24.34	176.67	176.33
298.15	77.34	77.51	147.46	145.64	43.96	43.42	182.89	182.85
300	77.80	78.28	148.15	148.15	44.44	44.44	183.03	182.74
400	100.51	100.91	173.72	173.84	69.49	69.54	191.77	191.53
500	119.50	119.82	198.27	198.47	99.13	99.23	202.61	202.40
600	134.70	134.95	221.45	221.71	132.87	133.02	215.15	214.97
700	146.80	146.99	243.16	243.45	170.21	170.41	229.05	228.89
800	156.53	156.69	263.42	263.73	210.73	210.98	244.03	243.90

#### 3.12. Transition state and kinetic

The transition state (TS) structure of photochromism reaction was obtained to using the QST3 method. Fully optimized structures for TS from calculations at B3LYP/6-311G(d,p) level of theory are shown in Fig. S5. The optimized TS structure for photochromism is a three-membered ring geometry, where the  $O_{24}$ - $C_{25}$  is very elongated (from 1.372 Å in the reactant to 1.659 Å in the TS), and the  $O_{22}$ - $C_{25}$  bond is reduced (from 2.896 Å in the reactant to 1.604 Å in the TS). The distance  $O_{24}$ - $O_{22}$  is reduced (from 2.711 Å in the reactant to 2.402 Å in the TS). The total energies, including the zero point vibrational energies and NBO charges were given in Table S8.

Estimated charges by the NBO method for the photochromism reaction show an increase in electron density on  $O_{22}$  and  $O_{24}$  (from -0.219 and -0.256 in the reactant to -0.323 and -0.360 in the TS). Also the electron density on the atom  $C_{25}$  decreases (from 0.226 in the reactant to 0.047 in the TS). Another important change is in  $C_8$  and  $C_{15}$  that are closer to the oxygen atoms in the TS, and become more positive in the TS, charge changes from 0.228 to 0.368 and from 0.189 to 0.309, respectively. TS structures were identified by existence of a single imaginary frequency in normal-mode results. The imaginary frequency implied that TS is a saddle point on the potential surface. Intrinsic reaction coordinate (IRC) calculations were performed to confirm that the transition state structures connect the reactant and product of the reaction (Fig. 10).

Frequency calculations allowed obtaining thermodynamic quantities in order to estimate activation parameters. The imaginary frequency that characterizes the TS is mainly associated with the benzaldehyde transfer from  $O_{22}$  to the  $O_{24}$ . After the analysis of



Fig. 9. Cyclic voltammogram of  $2\times 10^{-3}$  M title compound. Scan rate 100 mV  $s^{-1},$  electrolyte 0.1 M Bu4NBF4 in CH\_2Cl\_2.



Fig. 10. Reaction path curve of "trans" and "ana" form followed by IRC calculation.

vibration frequencies for the optimized geometry, the standard molar enthalpies, entropies and Gibbs free energies were obtained at different temperatures and some of results were given in Table S9 (Supplementary data). The first order rate constant k(T) was calculated using the transition state theory TST [70]. It was assumed that the transmission coefficient is equal to 1 as following equation:

$$k(T) = \left(\frac{k_{\rm B}T}{h}\right) \exp\left(-\frac{\Delta G^{\#}}{RT}\right) \tag{9}$$

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:

$$\Delta G^{\#} = \Delta H^{\#} - T \Delta S^{\#} \tag{10a}$$

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

$$\Delta H^{\#} = V^{\#} + \Delta Z P V E + \Delta E(T) \tag{10b}$$

 $V^{\#}$  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 250–400 K. The values of activation energy were obtained from the plots of calculated ( $-\log k$ ) vs. 1000/T (Fig. S6).  $\overline{E_a}$  was obtained from slope of cited plot and the data were presented in Table S10. By increasing of temperature, the rate constant increased too. When the temperature changed from 250 K to 400 K, k increased approximately  $10^{19}$  times.

#### 4. Conclusion

The FT-IR spectrum of the 4-((9,10-dioxo-9,10-dihydroanthracen-1-yl)oxy)benzaldehyde were recorded and analyzed. The molecular geometry and vibrational wavenumbers were calculated using DFT method and the optimized geometrical parameters (B3LYP) were in agreement with that of reported similar derivatives. The NBO analysis confirmed the ICT formed by the orbital overlap between n(O) and  $\sigma^*(C-H)$ ,  $\sigma^*(C-C)$ ,  $\pi^*(C-C)$ . The TD-DFT calculations on the molecule provided deep insight into their electronic structures and properties. In addition, the calculated UV-Vis results are all in good agreement with the experimental data. Theoretical <sup>1</sup>H and <sup>13</sup>C chemical shift values (with respect to TMS) which were reported and compared with experimental data, showed good agreement for <sup>1</sup>H and <sup>13</sup>C. MEP plots predict the most reactive part in the molecule. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives. The calculated vibrational normal-mode frequencies provide thermodynamic properties. QST3 method determined the transition structure of the benzaldehyde transfer reaction. IRC calculation provided the potential energy surface. Finally, the rate coefficient and activation energies of reaction were given, when the temperature changed from 250 K to 400 K. This study demonstrates that scaled DFT/ B3LYP calculations are a powerful approach for understanding the vibrational spectra of medium sized organic compound.

# Acknowledgment

Financial support of Damghan University is acknowledged.

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014.01. 040.

#### References

- [1] H.-H. Liua, Y. Chen, J. Phys. Org. Chem. 24 (2011) 517.
- [2] M.Å. Petersen, E. Deniz, M.B. Nielsen, S. Sortino, F.M. Raymo, Eur. J. Org. Chem. 25 (2009) 4333.
- [3] K. Kinashi, S. Nakamura, M. Imamura, K. Ishida, Y. Ueda, J. Phys. Org. Chem. 25 (2012) 462.
- [4] S.Y. Ju, D.-I. Kwon, S.-J. Minb, K.-D. Ahn, K.H. Park, J.-M. Kim, J. Photochem. Photobiol. A: Chem. 160 (2003) 151.
- [5] K.-D. Ahn, J.-H. Kang, K.-W. Chi, K.-D. Park, C.W. Lee, Bull. Korean Chem. Soc. 30 (2009) 1243.
- [6] F. Maurel, A. Perrier, D. Jacquemin, J. Photochem. Photobiol. A: Chem. 218 (2011) 33.
- [7] I.S. Park, E.-J. Heo, J.-M. Kim, Tetrahedron Lett. 52 (2011) 2454.
- [8] N.P. Gritsan, L.S. Klimenko, E.M. Shvartsberg, I.V. Khmelinski, E.P. Fokin, J. Photochem, Photobiol, A: Chem, 52 (1990) 137.
- [9] N.P. Gritsan, A. Kellmann, F. Tfibel, L.S. Klimenko, J. Phys. Chem. A 101 (1997) 794.
- [10] E.A. Pritchina, N.P. Gritsan, G.T. Burdzinski, M.S. Platz, J. Phys. Chem. A 111 (2007) 10483.
- [11] R. Born, W. Fischer, D. Heger, B. Tokarczyk, J. Wirz, Photobiol. Sci. 6 (2007) 552.
- [12] R.H. Thomson (Ed.), Naturally Occurring Quinones IV, Blackie Academic & Professional, London, 1997, p. 309.
- [13] D. Ajloo, B. Yoonesi, A. Soleymanpour, Int. J. Electrochem. Sci. 5 (2010) 459.
- [14] M.R. Dhananjeyan, Y.P. Milev, M.A. Kron, M.G. Nair, J. Med. Chem. 48 (2005) 2822.
- [15] M. Pickhardt, Z. Gazova, M. von Bergen, I. Khlistunova, Y. Wang, A. Hascher, E.-M. Mandelkow, J. Biernat, E. Mandelkow, J. Biol. Chem. 280 (2005) 3628.
- [16] J. Wang, R. Gao, Q. Li, S. Xie, J. Zhao, C. Wang, Chem. Biol. Drug Des. 80 (2012) 909
- [17] M. Vakili, S.F. Tayyari, A. Kanaani, A.-R. Nekoei, S. Salemi, H. Miremad, A.R. Berenji, R.E. Sammelson, J. Mol. Struct. 998 (2011) 99.
- [18] M. Vakili, A.-R. Nekoei, S.F. Tayyari, A. Kanaani, N. Sanatid, J. Mol. Struct. 1021 (2012) 102.
- [19] T.A. Koopmans, Physica 1 (1933) 104.
- [20] K.G. von Eschwege, J. Conradie, S. Afr. J. Chem. 64 (2011) 203.
- [21] K.G. von Eschwege, J.C. Swarts, Polyhedron 29 (2010) 1727.
- [22] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.02, Gaussian, Wallingford, 2004.
- [23] (a) A.D. Becke, Phys. Rev. A 38 (1988) 3098; (b) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785;
  - (c) A.D. Becke, J. Chem. Phys. 104 (1996) 1040.
- [24] GaussView 3.0. R. Dennington II, T. Keith, J. Millam, GaussView, Version 4.1.2, Semichem Inc., Shawnee Mission, KS, 2007.
- [25] J.B. Foresman, in: E. Frisch (Ed.), Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian, Gaussian Inc., Pittsburg, PA, 1996.
- [26] Genplot Package Computer Service, Cornell University, Utica, New York, 1990.
- R. Ditchfield, J. Chem. Phys. 80 (1984) 3265. 271
- [28] B.V.R. Murthy, Z. Kristallogr. 113 (1960) 445.
- [29] J.E. Gautrot, P. Hodge, D. Cupertino, M. Helliwell, New J. Chem. 31 (2007) 1585.
- [30] M. Kadarkaraisamy, D. Mukherjee, C.C. Soh, A.G. Sykes, Polyhedron 26 (2007) 4085.

- [31] V. Krishnakumar, R.J. Xavier, Spectrochim. Acta 61A (2005) 1799.
- [32] L. Lunazzi, M. Mancinelli, A. Mazzanti, J. Org. Chem. 74 (2009) 1345.
- [33] G. Rauhut, P. Pulay, J. Phys. Chem. 99 (1995) 3093.
- [34] M.W. Ellzy, J.O. Jensen, H.F. Hameka, J.G. Kay, D. Zeroka, Spectrochim. Acta 57A (2001) 2417.
- [35] J.O. Jensen, A. Banerjee, C.N. Merrow, D. Zeroka, J.M. Lochner, J. Mol. Struct. Theochem 531 (2000) 323.
- [36] Spectral Database for Organic Compounds SDBS, Institute of Advanced Industrial Science and Technology. [37] S. Gilmour, R.A. Montgomery, S.R. Marder, L.T. Cheng, A.K.Y. Jen, Y. Cai, J.W.
- Perry, L.R. Dalton, Chem. Mater. 6 (1994) 1603.
- [38] P. Sett, N. Paul, S. Chattopadhyay, P.K. Mallick, J. Raman Spectrosc. 30 (1999) 277.
- [39] P. Sett, S. Chattopadhyay, P.K. Mallick, Spectrochim. Acta 56A (2000) 855.
- [40] N.G.P. Roeges, A Guide to the Complete Interpretation of the Infrared Spectra of Organic Structures, Wiley, New York, 1994.
- [41] G. Varsanyi, Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives, Wiley, New York, 1974.
- [42] K.R. Ambujakshan, V.S. Madhavan, H.T. Varghese, C.Y. Panicker, O. Temiz-Arpaci, B. Tekiner-Gulbas, I. Yildiz, Spectrochim. Acta 69A (2008) 782.
- [43] A. Baran, B. Wrzosek, J. Bukowska, L.M. Proniewicz, M. Branska, J. Raman Spectrosc. 40 (2009) 436.
- [44] N.B. Colthup, L.H. Daly, S.E. Wiberly, Inroduction to Infrared and Raman Spectroscopy, third ed., Academic Press, Boston, 1990.
- [45] J.H.S. Greeb, Spectrochim. Acta 24A (1968) 1627 [46] E.D. Glendening, A.E. Reed, J.E. Carpenter, F. Weinhold, NBO Version 3.1, Gaussian Inc., Pittsburgh, PA.
- [47] C. James, A. Amal Raj, R. Reghunathan, I.H. Joe, V.S. Jayakumar, J. Raman Spectrosc. 37 (2006) 1381.
- [48] M. Szafran, A. Komasa, E.B. Adamska, J. Mol. Struct. Theochem 827 (2007) 101.
- [49] S. Sebastian, N. Sundaraganesan, Spectrochim. Acta 75A (2010) 941.
- [50] R. Meenakshi, Mol. Simul. 36 (2010) 425.
- [51] K. Wolinski, J.F. Hinton, P. Pulay, J. Am. Chem. Soc. 112 (1990) 8251.
- [52] H.O. Kalinowski, S. Berger, S. Braun, Carbon-13 NMR Spectroscopy, John Wiley & Sons, Chichester, 1988.
- [53] B. Osmiałowski, E. Kolehmainen, R. Gawinecki, Magn. Res. Chem. 39 (2001) 334.
- [54] E. Scrocco, J. Tomasi, Adv. Quantum Chem. 11 (1978) 115.
- [55] P. Politzer, J.S. Murray, in: D.L. Beveridge, R. Lavery (Eds.), Theoretical Biochemistry and Molecular Biophysics: A Comprehensive Survey. Protein, vol. 2, Adenine Press, Schenectady, NY, 1991 (Chapter 13).
- [56] E. Scrocco, J. Tomasi, Curr. Chem. 7 (1973) 95.
- [57] K. Fukui, Science 218 (1982) 747.
- [58] M.E. Casida, K.C. Casida, D.R. Salahub, Int. J. Quantum Chem. 70 (1998) 933.
- [59] E. Cances, B. Mennucci, J. Tomasi, J. Chem. Phys. 107 (1997) 3032.
- [60] H.-Y. Wang, L.-F. Chen, X.-L. Zhu, C. Wang, Y. Wan, H. Wu, Spectrochim. Acta 121A (2014) 355.
- [61] G. Yu, S. Yin, Y. Liu, Z. Shuai, D. Zhu, J. Am. Chem. Soc. 125 (2003) 14816.
- [62] X.N. Li, X.J. Liu, Z.J. Wu, H.J. Zhang, J. Phys. Chem. A 112 (2008) 11190.
- [63] (a) R.A. Hush, J. Chem. Phys. 28 (1958) 962; (b) R.A. Marcus, J. Chem. Phys. 24 (1956) 966;
- (c) R.A. Marcus, Rev. Mod. Phys. 65 (1993) 599. [64] T. Kamtekar, C. Wang, S. Bettington, A.S. Batsanov, I.F. Perepichka, M.R. Bryce, J.H. Ahn, M. Rabinal, M.C. Petty, J. Mater. Chem. 16 (2006) 3823.
- [65] D.A. Kleinman, Phys. Rev. 126 (1962) 1977.
- [66] T. Joseph, H.T. Varghese, C.Y. Panicker, T. Thiemann, K. Viswanathan, C.V. Alsenoy, J. Mol. Struct. 1005 (2011) 117.
- [67] M. Adant, L. Dupuis, L. Bredas, Int. J. Quantum Chem. 56 (2004) 497.
- [68] M.A. Palafox. Int. J. Ouantum Chem. 77 (2000) 661.
- [69] R.G. Parr, R.A. Donnelly, M. Levy, W.E. Palke, J. Chem. Phys. 68 (1978) 3801.
   [70] S.W. Benson, The Foundations of Chemical Kinetics, McGraw-Hill, New York, 1960