NBO, chemical reactivity, thermodynamic properties and hyperpolarizability analysis of aristolochic acid II

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Abstract

Alkaloids are a group of naturally occurring chemical compounds and show immense potential of medicinal uses in traditional systems. In this work, a computational study on an alkaloid aristolochc acidid II (AA II) is presented using density functional theory, B3LYP functional employing 6-311G (d,p) basis set. Natural bond orbital analysis has been carried out to investigate the various conjugative and hyperconjugative interactions within the molecule and their second-order stabilisation energy ($E^{(2)}$). The local nucleophilic reactivity descriptors such as Fukui functions (f_k^+, f_k^-), local softness (s_k^+, s_k^-) and electrophilicity indices (ω_k^+, ω_k^-) analyses have been carried out to determine the reactive sites within the molecule. The non-linear optical properties have been calculated using the same basis set. The calculated value of the first order hyperpolarisability (β_0), suggests that the investigated molecule is an attractive object in future for non-linear optical properties.

Keywords: AA II; DFT; NBO; chemical reactivity; hyperpolarizability.
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1. Introduction

Majority of drugs in use today are natural products, natural product mimics or semi synthetic derivatives. Therefore in recent times, focus on plant research has increased all over the world and large body of evidence has been collected to show immense potential of medicinal plants used in various traditional systems. Plants are sources of natural antioxidants, and some of the compounds have significant antioxidative properties and health benefits. Aristolochic acids (AAs) which mainly include aristolochic acid I (AA I), aristolochic acid II (AA II) and aristolochic acid III (AA III) are normally present in *Aristolochia* and *Asarum* of *Aristolochiaceae* [1]. In oriental medicine the fruit of *Aristolochia* is given for cough and dyspnea. Their roots have biological functions including treatment of stomach-ache,

toothache, eczema, hypertension relief, rheumatism relief, leukocyte enhancement, edema therapy, poisonous snake bites as well as analgesic and diuretic effects [2,3]. In the family of natural products, the alkaloids occupy a unique place and provide challenging problems for structural elucidation, synthetic and biosynthetic studies. Because of their very complex structure and unique places the determination of their constitution and the discovery of the methods producing them synthetically offer attractive problems to the chemist and though a great deal has been accomplished much still remains to be done in this field. Vibrational spectroscopy is a very valuable method for studying the dynamical behavior and to gain insight into the electronic structures of alkaloids at microscopic level [4]. However, both the Raman and IR are the best traditional methods for the vibrational analysis and particularly for the non-destructive characterization of the substances [5], but in the recent years there has been interest in the application of *ab initio* calculations to the alkaloids as it provide the additional vibrational spectroscopic data [3-6].

In the present work the chemical reactivity descriptors, thermodynamic properties and the natural bond orbitals (NBOs) analysis of an alkaloid aristolochic acid II have been communicated. The aim of this study was to determine the stabilization energy when the system acquires an additional charge from the environment and the direction of the charge transfer. Similarly, the variation of the thermodynamic properties with the temperature and, hybridization, conjugation and charge transfer in the polyatomic wave functions theoretically using *ab initio* HF and density functional theory (DFT) [7]. We had presented some spectroscopic analysis on the title molecule in our previous work [8]. The crystal structure and optimized structure of AA II are as shown in the Figure 1a and b.
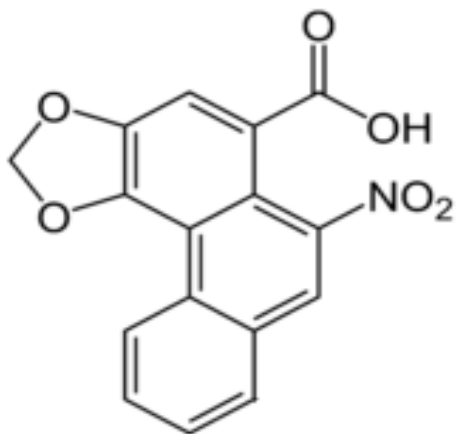
Fig. 1(a): Crystal structure of AA II.   **Fig. 1(b):** Optimized structure of AA II.
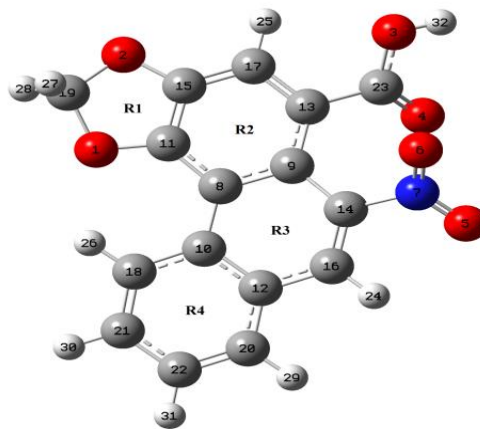
2. Materials and Methods

2.1 Computational Details

Geometry optimization has been performed as the first task of the computational work. The geometric parameters available from the PubChem data base [9] have been used as the basis for the optimization. These optimized parameters were computed by *ab intio* HF and the DFT using Gaussian 09 [10] program package employing B3LYP/6-311G (d,p) basis set. The DFT calculations were mainly carried out in the

frame-work of the Becke–Lee-Yang-Parr [B3LYP] functional, in which the exchange functional is a local spin density exchange with Becke gradient correction [11] and the correlation functional is that of Lee, Yang and Parr with both local and nonlocal terms [12,13].

3. Results and Discussion

3.1 Natural bond Orbital (NBO) Analysis

NBO analysis is one of the efficient methods for studying hybridization, conjugative interactions, covalence effects and charge transfer in polyatomic wave functions [4]. In the present work, utilizing the second-order micro-disturbance theory analysis, we have reported some of the electron donor orbital, acceptor orbital and the interacting stabilization energy. Higher the value of stabilization energy $E^{(2)}$ more is the intensity of the interaction between electron donors and electron acceptors, i.e. the more donating tendency from electron donors to electron acceptors. The hyperconjugative interaction energy was deduced from the second-order perturbation approach [14-16].

$$E^{(2)} = -\frac{n_\sigma \langle \sigma|F|\sigma \rangle^2}{E_{\sigma*}-E_\sigma} = -n_\sigma \left| \frac{F_{ij}^2}{\Delta E} \right|$$

where $\langle \sigma|F|\sigma \rangle^2$, or F_{ij}^2 is the Fock matrix element between i and j NBO orbital, E_σ and $E_{\sigma*}$ are the energies of σ and $\sigma*$ NBO's, and n_σ is the population of the donor orbital. The larger the $E^{(2)}$ value the more intensive is interaction, the greater the extent of conjugation of the whole system [16]. Hyperconjugation may be given as a stabilizing effect that arises from overlap between an occupied orbital with another neighboring electron deficient orbital when these orbitals are properly oriented. The most important interaction between ''filled'' (donor) Lewis type NBOs and ''empty'' (acceptor) non-Lewis NBOs are reported in Table 1.

There occurs a strong intramolecular hyperconjugative interactions of π electrons of the rings R2 and R3 from C11 - C15, C13 - C17, C10 - C12 and C14 - C16 to the $\pi*$(C8 - C9) bond of which increases the electron density 0.474e leading to the stabilization. This enhanced the further conjugation of the $\pi*$(C8 - C9) NBO mainly with $\pi*$(C10 – C12) and $\pi*$(C14 – C16) resulting to the high stabilization of 236.16 and 134.76 kcal/mol, respectively. Also, there occur some another hypercinjugative interactions of π electrons from C13 – C17 → $\pi*$(C11 – C15) with ED 0.40135e, C14 – C16 → $\pi*$(O5 – N7) with ED 0.60349e, C18 – C21 → $\pi*$(C10 – C12) with ED 0.44633e and C20 – C22 → $\pi*$(C18 – C21) with ED 0.27488e leading to the stabilization energies 21.06, 16.48, 18.62 and 18.77 kcal/mol, respectively. Similarly, the enhanced NBOs $\pi*$(C11 – C15) conjugate with $\pi*$(C13 – C17) in ring R2 which further conjugates with $\pi*$(O4 – C23) of the carboxyl group leading to the corresponding stabilization energies 276.35 and 112.33 kcal/mol, respectively. The electron donation related to the resonance in the molecule is from LP(2) O3 to antibonding acceptor $\pi*$(O4 – C23) of carboxyl group (41.00 kcal/mol) and from LP(2) O6 to $\pi*$(O5 – N7) of NO$_2$ group (168.74 kcal/mol). The interactions are mainly confined between the rings and the lone pair electron groups. These charge transfer in the system lead to the structure activity of the molecule. A comparison of the NBO and Mullikan charges is given in the Table 2.

Table 1: Second order perturbation theory analysis of Fock matrix in NBO basis for AA II.

Donor NBIO(i)	ED (i)/e	Acceptor NBO(j)	ED (j)/e	E(2)[a] (kcl/mol)	[E(j) –E(i)][b]	F(i,j)[c]
LP(2)O1	1.85366	π^* (C11 – C15)	0.40135	23.22	0.35	0.087
LP(2)O2	1.85651	π^* (C11 – C15)	0.40135	23.59	0.35	0.086
LP(2)O3	1.82127	π^* (O4 – C23)	0.24140	41.00	0.36	0.111
LP(2)O4	1.83912	σ^*(O3 - C23)	0.09844	32.38	0.61	0.128
		σ^*(C13 - C23)	0.06750	18.44	0.68	0.102
LP(2)O5	1.89423	σ^*(O6 – N7)	0.07135	19.19	0.71	0.105
		σ^*(N7 – C14)	0.10978	14.26	0.55	0.079
LP(2)O6	1.89355	σ^*(O6 – N7)	0.07135	18.60	0.73	0.105
		π^*(O5 – N7)	0.60349	168.74	0.15	0.144
σ(C11 - C15)	1.97681	σ^*(C8 - C11)	0.02801	6.07	1.27	0.079
σ(C14 - C16)	1.97140	σ^*(C9 - C14)	0.03163	5.49	1.24	0.074
σ(C16 – H24)	1.97338	σ^*(C9 - C14)	0.03163	6.26	1.02	0.072
π(C8 - C9)	1.58253	σ^*(O1 - C11)	0.02832	6.00	0.99	0.069
π(C10 – C12)	1.56437	π^* (C8 – C9)	0.47400	16.91	0.26	0.060
		π^* (C14 – C16)	0.22748	16.78	0.28	0.065
		π^* (C18 – C21)	0.27488	17.31	0.28	0.065
		π^* (C20 – C22)	0.27301	17.26	0.28	0.065
π(C11 – C15)	1.63802	π^* (C8 – C9)	0.47400	17.68	0.30	0.067
		π^* (C13 – C17)	0.36737	20.25	0.31	0.071
π(C13 – C17)	1.68334	π^* (O4 – C23)	0.24140	17.24	0.30	0.065
		π^* (C8 – C9)	0.47400	18.48	0.28	0.067
		π^* (C11 – C15)	0.40135	21.06	0.27	0.069
π(C14 – C16)	1.77190	π^* (O5 – N7)	0.60349	16.48	0.17	0.052
		π^* (C8 – C9)	0.47400	13.55	0.30	0.061
		π^* (C10 – C12)	0.44633	12.99	0.31	0.060
π(C18 – C21)	1.68756	π^* (C10 – C12)	0.44633	18.62	0.28	0.067
		π^* (C20 – C22)	0.27301	18.46	0.29	0.066
π(C20 – C22)	1.69812	π^* (C10 – C12)	0.44633	18.47	0.29	0.067
		π^* (C18 – C21)	0.27488	18.77	0.29	0.067
π^*(C8 - C9)	0.47400	π^* (C10 – C12)	0.44633	16.36	0.28	0.061
		π^* (C11 – C15)	0.40135	23.40	0.26	0.070
		π^* (C13 – C17)	0.36737	18.20	0.28	0.064
		π^*(C10 – C12)	0.44633	236.16	0.01	0.074
		π^*(C14 – C16)	0.22748	134.76	0.02	0.072
π^*(C11 – C15)	0.40135	π^*(C13 – C17)	0.36737	276.35	0.01	0.084
π^*(C13 – C17)	0.36737	π^*(O4 – C23)	0.24140	112.33	0.01	0.063

[a] $E^{(2)}$ means energy of hyper conjugative interaction (stabilization energy).
[b] Energy difference between donor (i) and acceptor (j) NBO orbitals.
[c] F(i,j) is the Fock matrix element between i and j NBO orbitals.

Table 2: Comparison between NBO and Mullikan charges (esu) of AA II.

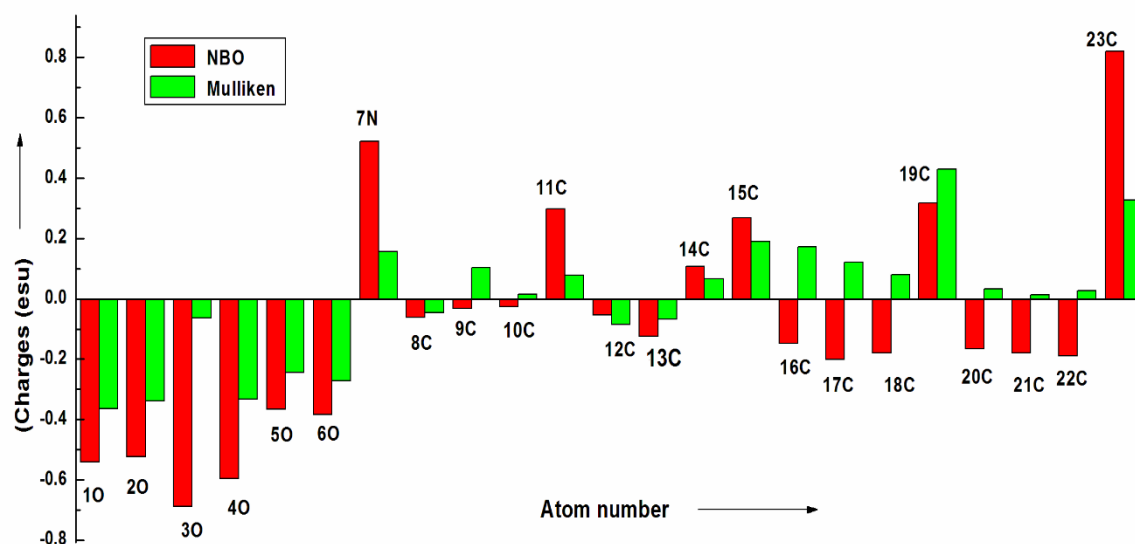| Atom No	NBO charges	Mulliken charges	Atom No	NBO charges	Mulliken charges
1 O	-0.541	-0.364			
2 O	-0.523	-0.339			
3 O	-0.688	-0.064	14 C	0.108	0.067
4 O	-0.595	-0.333	15 C	0.269	0.189
5 O	-0.367	-0.245	16 C	-0.147	0.172
6 O	-0.384	-0.271	17 C	-0.201	0.122
7 N	0.522	0.156	18 C	-0.180	0.080
8 C	-0.061	-0.045	19 C	0.318	0.429
9 C	-0.032	0.103	20 C	-0.165	0.032
10 C	-0.026	0.016	21 C	-0.179	0.014
11 C	0.298	0.078	22 C	-0.189	0.027
12 C	-0.054	-0.084	23 C	0.820	0.328
13 C	-0.124	-0.067			

Fig. 2: Correlation between NBO and Mulliken charges.

3.2 Chemical Reactivity

3.2 (a) Global Reactivity Descriptors

Electrophilicity and hardness are two important molecular properties, which are useful for interpreting and understanding the stability and reactivity of molecular system [17]. According to the Hohenberg and Kohn (HK), theorems [7], the energy of the basic state of an electronic system is a functional of electron density. On the basis of Koopman's theorem [17], global reactivity descriptors: electronegativity (χ),

chemical potential (μ), global hardness (η), global softness (S) and global electrophilicity index (ω) were calculated using the energies of frontier molecular orbitals E_{HOMO}, E_{LUMO} and given by relations (1) - (5) [18-20].

$$\chi = -\frac{1}{2}[E_{HOMO} + E_{LUMO}] \tag{1}$$

$$\mu = -\chi = \frac{1}{2}[E_{HOMO} + E_{LUMO}] \tag{2}$$

$$\eta = \frac{1}{2}[E_{LUMO} - E_{HOMO}] \tag{3}$$

$$S = \frac{1}{2}\eta \tag{4}$$

$$\omega = \frac{\mu^2}{2\eta} \tag{5}$$

$$\Delta N_{max} = -\frac{\mu}{\eta} \tag{6}$$

According to Parr et al., electrophilicity index (ω), a positive and finite quantity, is a global reactivity index similar to the chemical hardness (a measure of the resistance of a system to transfer charge), and chemical potential. This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge (ΔN) from the environment up to saturation. The direction of the charge transfer is completely determined by the electronic chemical potential of the molecule because an electrophile is a chemical species capable of accepting electrons from the environments. Therefore its energy must decrease upon accepting electronic charge and its electronic chemical potential must be negative. The energies of frontier energy levels (E_{HOMO}, E_{LUMO}), energy band gap (ΔE), electronegativity (χ) that representing the tendency of atoms or molecules to attract electrons; chemical potential (μ), global hardness (η), global softness (S), global electrophilicity index (ω), and additional electronic charge (ΔN) for AA II are listed in the Table 3. The calculated high value of electrofilicity index (ω) shows that the molecule behaves as a strong electrophile.

Table 3: Calculated E_{HOMO}, E_{LUMO}, energy band gap (ΔE), electronegativity (χ), chemical potential (μ), global hardness (η), global softness (s), global electrophilicity index (ω) and additional electronic charge (ΔN_{max}) (in eV) for AA II , using B3LYP/6-31G (d,p).

E_{HOMO}	E_{LUMO}	ΔE	μ	η	S	ω	ΔN_{max}
-6.113904	- 2.396963	3.716941	-4.267835	1.858471	0.269038	4.900378	2.296299

3.2 (b) Local Reactivity Descriptors

Using Hirshfeld population analysis of neutral, cation and anion state of molecule, Fukui functions (f_k^+, f_k^-, f_k^0) [20, 21], are calculated at same calculation method B3LYP/6-31 G (d,p) using following relations (7-9):

$$f_k^+ = [q(N+1) - q(N)] \text{ for nucleophilic attack} \tag{7}$$

$$f_k^- = [q(N) - q(N-1)] \text{ for electrophilic attack} \tag{8}$$

$$f_k^0 = \frac{1}{2}[q(N+1) - q(N-1)] \text{ for radical attack} \tag{9}$$

where N, N-1 and N+1 are total electrons present in neutral, cation and anion state of molecule, respectively.

Local softnesses (s_k^+, s_k^-, s_k^0) and local electrophilicity indices (ω_k^+, ω_k^-, ω_k^0), also used to describe the reactivity of atoms in molecule, are calculated using the following equations (10) and (11):

$$s_k^+ = Sf_k^+, \; s_k^- = Sf_k^-, \; s_k^0 = Sf_k^0 \tag{10}$$

$$\omega_k^+ = \omega f_k^+, \; \omega_k^- = \omega f_k^-, \; \omega_k^0 = \omega f_k^0 \tag{11}$$

where +, −, 0 signs show nucleophilic, electrophilic and radical attack, respectively.

Table 4: Hirshfelf atomic charges (in esu), Fukui functions (f_k^+, f_k^-); Local softness (s_k^+, s_k^-); and local electrophilicity indices (ω_k^+, ω_k^-); in eV for atomic sites of AA II, using Hirshfeld population analysis at B3LYP/6-31G (d,p) level.

Atom no.	Hirshfeld atomic charges			Fukui functions		Local softness		Local electrophilicity indices	
	q_N	q_{N+1}	q_{N-1}	f_k^+	f_k^-	s_k^+	s_k^-	ω_k^+	ω_k^-
1 O	-0.137056	-0.082403	-0.154852	0.05465	0.01779	0.0147	0.0048	0.2678	0.0872
2 O	-0.154125	-0.084260	-0.180316	0.06986	0.02619	0.0188	0.0070	0.3424	0.1283
3 O	0.014549	0.054444	-0.024939	0.03989	0.03948	0.0107	0.0106	0.1955	0.1935
4 O	-0.285351	-0.247806	-0.310391	0.03754	0.02504	0.0101	0.0067	0.1840	0.1227
5 O	-0.188738	-0.146976	-0.272371	0.04176	0.08363	0.0112	0.0225	0.2046	0.4098
6 O	-0.197151	-0.168658	-0.278778	0.02849	0.08162	0.0077	0.0220	0.1396	0.4000
7 N	0.235014	0.239420	0.193255	0.00440	0.04175	0.0012	0.0112	0.0216	0.2046
8 C	-0.004447	0.007625	-0.015539	0.01207	0.01109	0.0032	0.0030	0.0592	0.0544
9 C	-0.001680	0.024782	-0.005068	0.02646	0.00338	0.0071	0.0009	0.1297	0.0166
10 C	0.002314	0.017857	-0.029614	0.01554	0.03192	0.0042	0.0086	0.0762	0.1565
11 C	0.067660	0.115375	0.035707	0.04771	0.03195	0.0128	0.0086	0.2338	0.1566
12 C	-0.003587	0.019794	-0.024961	0.02338	0.02137	0.0063	0.0058	0.1146	0.1047
13 C	-0.019426	0.041108	-0.050936	0.06053	0.03151	0.0163	0.0085	0.2966	0.1544
14 C	0.037710	0.073211	-0.007816	0.03550	0.04552	0.0096	0.0122	0.1740	0.2231
15 C	0.060119	0.117917	0.026964	0.05779	0.03315	0.0155	0.0089	0.2832	0.1625
16 C	0.032000	0.105890	-0.068122	0.07389	0.10012	0.0199	0.0269	0.3621	0.4906
17 C	0.027244	0.077415	-0.035180	0.05017	0.06242	0.0135	0.0168	0.2459	0.3059
18 C	0.001778	0.029849	-0.037889	0.02807	0.03966	0.0076	0.0107	0.1376	0.1944
19 C	0.252942	0.342971	0.204487	0.09002	0.04845	0.0242	0.0130	0.4412	0.2374
20 C	0.019442	0.075432	-0.037948	0.05599	0.05739	0.0151	0.0154	0.2744	0.2812
21 C	0.016208	0.092320	-0.075592	0.07611	0.0918	0.0205	0.0247	0.3730	0.4499
22 C	0.014773	0.073505	-0.047009	0.05873	0.06178	0.0158	0.0166	0.2878	0.3028
23 C	0.209756	0.221156	0.196862	0.0114	0.01289	0.0031	0.0035	0.0559	0.0632

3.3 Thermodynamic Properties

Computation of thermodynamic properties of molecules is important for both thermochemistry and chemical equilibrium. Statistical thermodynamics with the two key ideas, Boltzmann distribution and the partition function leads to the derivation of the equations utilized for computing thermochemical data in Gaussian programs. The standard thermodynamic functions: heat capacity ($C_{p,m}^o$), entropy (S_m^o) and enthalpy (H_m^o) together with the total energy, zero point energy, rotational constants, dipole moment were obtained directly from the output of DFT calculation employing 6-311G (d,p) basis set and listed in Tables 5a and b.

As observed from the table, the values of $C_{p,m}^o$, S_m^o and H_m^o increase with the increase of temperature from 100 K to 900 K which is attributed to the enhancement of molecular vibration while the temperature increases. The correlation between temperature and these thermodynamic properties are given in Fig. 3.

Table 5(a): Theoretically calculated thermodynamic properties at different temperatures using 6-311G (d,p) basis set.

Temperature (K)	Enthalpy (kJ/mol)	Specific heat (J/mol-K)	Entropy (J/mol-K)
100	600.0808	109.4366	349.5692
200	615.3002	195.5655	457.4258
300	639.3226	284.6956	556.9808
400	671.9977	366.7323	652.7906
500	712.2009	434.9499	744.0818
600	758.5195	489.2314	829.8888
700	809.6702	532.1265	909.9358
800	864.6581	566.3607	984.4193
900	922.7266	594.0700	1053.757

The correlation equations are as follows:

$$H_m^o = 583.65002 + 0.10323\ T + 3.07745\ \text{x}10^{-4}T^2 \qquad (R^2 = 0.99952) \qquad (12)$$
$$C_{p,m}^o = -2.98254 + 1.12581\ T - 5.14425\ \text{x}10^{-4}\ T^2 \qquad (R^2 = 0.99957) \qquad (13)$$
$$S_m^o = 238.13449 + 1.14381 - 2.63687\ \text{x}10^{-4}\ T^2 \qquad (R^2 = 0.99999) \qquad (14)$$

These thermodynamic relations would provide useful information for the study of thermodynamic energies and estimate directions of chemical reactions according to the second law of thermodynamics in thermochemical field. Further, these equations could be utilized in predicting the Gibbs free energy, which would help in the judgment of spontaneity of the reactions. [22].

3.4 Nonlinear Optical properties (NLO)

Nonlinear optics (NLO) deals with the interactions of applied magnetic fields in various materials to generate new magnetic field altered in phase, frequency, amplitude or other physical properties [23]. Some organic substances with π electronic system exhibit the largest known nonlinear coefficients and show promise for thin fabrication, allowing the enormous function and cost integrated electronic circuitry.
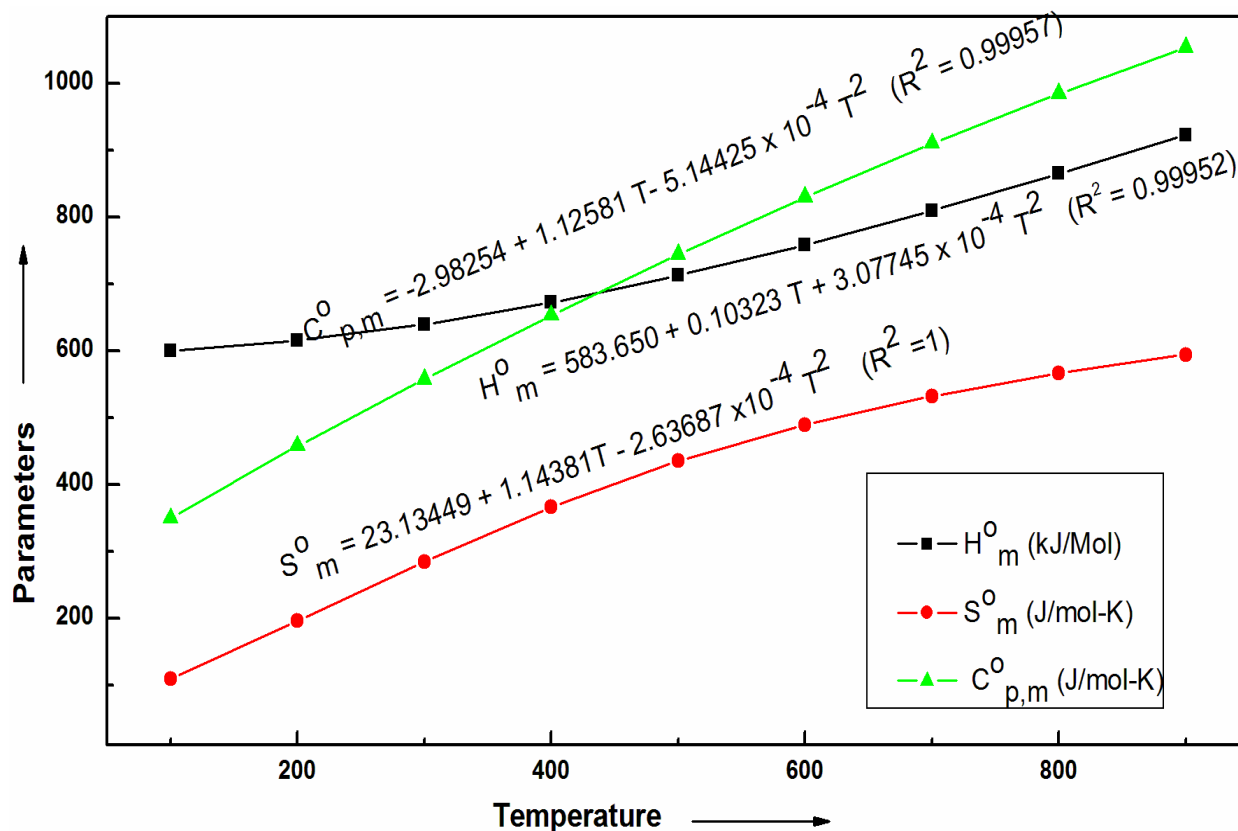
Fig. 3: Correlation between the thermodynamic parameters with the temperature.

Table 5(b): Theoretically calculated thermodynamic properties at room temperature using   6-311G (d,p) basis set.

Thermodynamic properties	DFT (B3LYP)	HF
Total energy (eV)	-30513.38103	-30336.08362
Zero-point energy (kJ/mol)	142.05075	151.82499
Rotational constants (GHz)	0.33647	0.33647
	0.27097	0.27097
	0.15671	0.15671
Dipole moment (D)	6.2937	6.8561
Entropy (J/mol-K)	555.17088	498.49426
Enthalpy (kJ/mol)	638.80014	673.31022
Specific heat (J/mol-K)	283.07796	256.55586

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 Kleinmann symmetry [21]. It can be given in the lower tetrahedral format. It is obvious that the lower part of the 3×3×3 matrix is a tetrahedral. The components of β_0 are defined as the coefficients in the Taylor series expansion of the

energy in the external electric field. When the external electric field is weak and homogeneous this expansion becomes:

$$E = E^0 - \mu_i F_i - \frac{1}{2}\alpha_{ij}F_iF_j - \frac{1}{6}\beta_{ijk}F_iF_jF_k \ .....$$

where E^0 is the energy of the unperturbed molecules, F_i is the field at the origin and μ_i, α_{ij}, β_{ijk} are the components of dipole moment, polarizability, and first hyperpolarizability respectively. The total dipole moment (μ_0), the mean polarizability ($|\alpha_0|$), the anisotropy of the polarizability ($\Delta\alpha$) and the total first hyperpolarizability (β_0) using x, y, z components are defined as [24]:

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2} \tag{15}$$

$$|\alpha_0| = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) \tag{16}$$

$$\Delta\alpha = 2^{-1/2}\left[\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2\right]^{1/2} \tag{17}$$

$$\beta_0 = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2} \tag{18}$$

Where

$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$
$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$
$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$

Since the x, y, z components of $|\alpha_0|$, $\Delta\alpha$ and β_0 of Gaussian 09 output are reported in a atomic mass unit (a.u.), the calculated values have been converted into electrostatic unit (esu) (for $|\alpha_0|$: 1 a.u. = 0.1482×10^{-24} esu; for β_0: 1 a.u. = 0.086393×10^{-31} esu) and listed in the Table 6. The high value of β_0, one of the key factors in an NLO system, supports that the investigated molecule will show good NLO response.

Table 6: Dipolemoment (μ Debye), polarizability (α x10^{-24}esu) and first order hyperpolarizability (β_0 x10^{-31}esu).

Dipole moment			Polarizability			Hyperpolarizability		
	DFT	HF		DFT	HF		DFT	HF
μ_x	-5.2839	-5.2243	α_{xx}	-119.1408	-118.3740	β_{xxx}	27.3548	31.7449
μ_y	4.0465	3.7945	α_{yy}	-121.7131	-122.2665	β_{yyy}	53.8593	47.8559
μ_z	0.1350	0.2183	α_{zz}	-136.8908	-138.6496	β_{zzz}	5.8486	6.4994
μ_0	6.6567	6.4607	α_{xy}	10.6612	12.0501	β_{xyy}	-71.5489	-71.1348
			α_{xz}	-2.7854	-2.4720	β_{xxy}	37.2794	38.8391
			α_{yz}	0.7627	0.7135	β_{xxz}	-17.6840	-16.7678
			$|\alpha_0|$	-125.9149	-126.4300	β_{xzz}	7.6975	8.5779
			$\Delta\alpha$	207.6443	206.4903	β_{yzz}	16.6563	18.0840
				30.7314	30.5606	β_{yyz}	8.8145	9.7722
						β_{xyz}	-9.5344	-10.3423
						β_0	9.8355	9.4355

4. Conclusion

Computational study proves that NBO analysis and NLO properties of the investigated molecule are successfully predicted by the B3LYP/6-311G (d,p) method. The $\pi \rightarrow \pi^*$ interactions are responsible for

the conjugation of respective π-bonds within aromatic rings, rings and C=O, NO_2 groups, which stabilized the molecule with maximum energy $\sim$ 21.06, 17.24 and 16.48 kcal/mol, respectively. The electron donation related to the resonance interaction in the molecule is mainly confined between the rings and the lone pair groups leading to the maximum energy 168.74 kcal/mol. The calculated high value of electrofilicity index (ω) is in agreement that the molecule behaves as a global electrophile. The compound exhibits strong effective ICT due to the movement of the π-electron cloud from donor to acceptor and shows second-order nonlinearity. The value of first order hyperpolarisability (β_0) shows that the title molecule can be used as an attractive material for NLO applications.

Acknowledgements

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