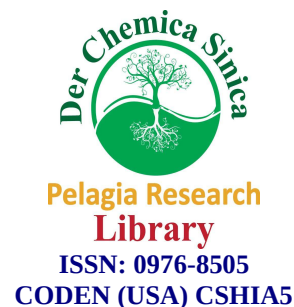




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HOMO, LUMO analysis and first order hyperpolarizability of 2-amino-5-chloro benzophenone using computational methods

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ABSTRACT

In recent days organic single crystals are gaining important due to good optical behavior. In this work nonlinear optical 2-Amino-5 Chloro Benzophenone (2A5CB) is studied using vibrational and density functional theory. Meanwhile DFT computations have been performed to calculate the first order hyperpolarizability of this novel molecular system and related properties of 2A5CB using B3LYP/6-31+G (d,p) basis set, based on the finite- field approach. The optimized geometric bond lengths and bond angles obtained by using DFT were also calculated and depicted.

INTRODUCTION

During the past decades organic nonlinear optical materials have been attracted much attention because of their optical nonlinearity, fast response, relatively low cost, ease of fabrication and integration into devices[1-2]. NLO materials have gained attention in recent years with respect to their future potential applications in the field of optoelectronic such as optical communication, optical computing, optical switching and dynamic image processing [3].

Experimental measurements and theoretical calculations on molecular hyperpolarizability β become one of the key factors in the second – order NLO materials design. Theoretical determination of hyperpolarizability is quite useful both in understanding the relationship between the molecular structure and nonlinear optical properties.

The vibrational spectral studies of the molecule can provide deeper knowledge about the relationships between molecular architecture, nonlinear response and hyperpolarizability. In this study molecular geometry, optimized parameters are computed and the performance of the computational method for B3LYP at 6-31+G (d,p) basis set[4]. This method predicts relatively accurate molecular structure with moderate computational effort. Recently, vibrational spectra combined with DFT calculations have been used as an effective tool in the study of NLO active compounds [5]. This study is extended to determine the electric dipole moment μ_{tot} , isotropic polarizability α_{tot} and the first hyperpolarizability β_{tot} of the title compound.

Organic molecules with conjugated π electron system are known to exhibit extremely large optical nonlinear responses in terms of their molecular hyperpolarizabilities. Both theoretical and experimental studies have shown that large polarizabilities generally arise from a combination of strong electron donor and acceptor positioned at opposite ends of a suitable conjugation path and hyperpolarizability values depending not only on the strength of donor and acceptor groups but also on the path length between them [3].

Computational Details:

In the present investigation we adopted density functional theory (DFT) to theoretically predict IR spectrum. Thermo dynamical parameter and first order hyper polarizability. DFT studies have been accepted as a popular approach for molecular computation.

The entire calculations were performed using Gaussian 03, Revision B-01 [6] program package invoking gradient geometry optimization. The optimized geometry corresponding to the minimum on the potential energy surface was first obtained by semi empirical method with AM1 and PM3 functional, and then by DFT Becke- Lee-Young – Parr composite of exchange correlation (B3LYP) functional with the STO-3G, 3-21G, 6-31G basis set. Finally, the geometry optimizations and frequency calculations were carried out at the same level by employing DFT-B3LYP hybrid functional and 6-31+G (d,p) basis set.

RESULTS AND DISCUSSION

Molecular Geometry:

The optimized molecular geometry represents an isolated molecule under ideal conditions with a stationary point at the potential energy surfaces; the convergence was confirmed by observing no imaginary vibrational wave numbers. From table shows the selected bond lengths and bond angles for 2A5CB molecules unit in solid phase along with the B3LYP/6-31+G (d,p) optimized molecule⁵. The optimized structure parameters of 2A5CB calculated by DFT levels with the B3LYP/6-31+G (d,p) basis set is listed in Table 1 in accordance with the atomic numbering scheme given in Fig 1

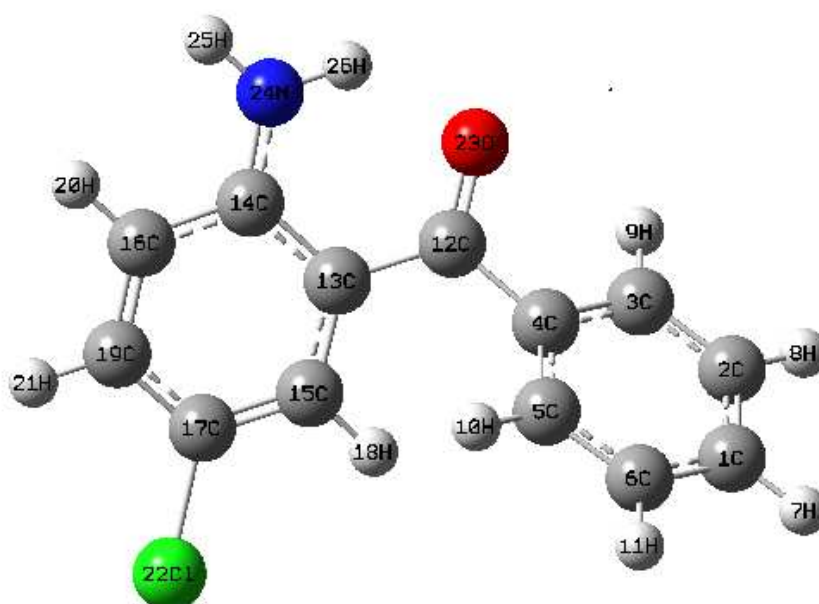


Fig. 1 Atom numbering scheme adopted in this study for 2- Amino-5 Chloro Benzophenone

Table 1 Geometrical Parameters optimized in 2- Amino-5 Chloro Benzophenone

Parameters	B3LYP/ 6-31G(d,p)
Bond Length	
C ₁ -C ₂	1.40144
C ₁ -C ₅	1.39931
C ₁ -H ₇	1.08537
C ₂ -C ₃	1.39532
C ₃ -C ₄	1.40798
C ₃ -H ₉	1.08409
C ₅ -C ₆	1.39872
C ₅ -H ₁₀	1.08428
C ₁₂ -O ₂₃	1.26802
C ₁₂ -C ₄	1.496011
C ₁₂ -C ₁₃	1.47276
C ₁₄ -C ₁₃	1.43768
C ₁₄ -C ¹⁶	1.42005
C ₁₄ -N ₂₄	1.36365
N ₂₄ -H ₂₆	1.01396
N ₂₄ -H ₂₅	1.00624
C ₁₇ -Cl ₂₂	1.83049
C ₁₇ -C ₁₅	1.37994
C ₁₇ -C ₁₉	1.40058

Bond angle	
C ₁ -C ₂ -C ₆	119.85075
C ₂ -C ₃ -C ₄	120.53366
C ₃ -C ₄ -C ₅	119.00198
C ₅ -C ₆ -C ₁	120.17322
C ₁₄ -C ₁₆ -H ₂₀	118.75084
H ₂₅ -N ₂₄ -H ₂₆	121.35140
Cl ₂₂ -C ₁₇ -C ₁₅	119.66471
Cl ₂₂ -C ₁₇ -C ₁₉	119.07477
C ₁₆ -C ₁₄ -N ₂₄	119.74189

Dihedral angles	
H ₁₁ -C ₆ -C ₁ -H ₇	0.84174
H ₇ -C ₁ -C ₂ -H ₈	-0.03845
H ₈ -C ₂ -C ₃ -H ₉	-1.23365
H ₉ -C ₃ -C ₄ -C ₁₂	-2.74049
O ₂₃ -C ₁₂ -C ₁₃ -C ₁₄	-14.77987
N ₂₄ -C ₁₄ -C ₁₃ -C ₁₂	2.00279
N ₂₄ -C ₁₄ -C ₁₆ -H ₂₀	-1.09342
C ₅ -C ₄ -C ₃ -C ₂	1.98673
C ₆ -C ₁ -C ₂ -C ₃	-0.13047
C ₄ -C ₅ -C ₆ -C ₁	-0.42339

Dipole moment and Hyperpolarizability:

Theoretical calculation provides another method to investigate substantial characters of materials. As hyperpolarizability is difficult to measure directly, computational calculation is an alternate choice. The first order hyperpolarizability β_0 of title molecular system and related properties (μ , β_0) of 2A5CB are calculated using B3LYP/6-31+G(d,p) basis set, 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 order hyperpolarizability is a third rank tensor that can be described by a 3x3x3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [7-8]. It can be given in the lower tetrahedral format. It is obvious that the lower part of 3x3x3 matrices is a tetrahedral.

The total static dipole moment μ and the mean first hyperpolarizability β_0 , using the x, y, z components they are defined as

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

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

Table 2 Calculated of all β components and β_{tot} value of 2A5CB

Parameters	B3LYP/6-311+G(d,p)
β_{xxx}	295.47097
β_{xyy}	-76.57960
β_{xyv}	47.871958
β_{vyv}	-9.620273
β_{xxx}	-17.927387
β_{vyz}	240.62797
β_{xzz}	-43.1433581
β_{vzz}	243.363915
β_{zzz}	-22.1690034
β_{tot}	3.5724×10^{-30}

Parameters	B3LYP/6-311+G(d,p)
μ_x	-0.2817
μ_y	1.1394
μ_z	1.2083
μ_{tot}	1.684 debye

$$\begin{aligned}\beta_x &= \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \\ \beta_y &= \beta_{yyy} + \beta_{xyx} + \beta_{yzz} \\ \beta_z &= \beta_{zzz} + \beta_{xxz} + \beta_{yyz}\end{aligned}$$

The total molecular dipole moment and mean first hyperpolarizability of 2A5CB is 1.6845 debye and 3.5724×10^{-30} esu respectively shown in Table 2. The connection between the electric dipole moments of an organic molecule having donor – acceptor substituent and first order hyperpolarizability is widely recognized in the literature.

Mulliken population analysis:

The charge distributions calculated by the mulliken method for the equilibrium geometry of 2A5CB. The charge distribution on the molecule has an important influence on the vibrational spectra. The corresponding Mullikens with the basis set B3LYP/6-31+G (d,p) are shown in Table 3.

In 2A5CB the basis set become more negative, while their natural atomic charges show positive values. The above result shows that the natural atomic charges are more sensitive to the charges in the molecular structure than Mulliken's net charge.

Table.3 Charge distribution calculated by the Mulliken method for 2A5CB

Atoms	Atomic charges with B3LYP	Atoms	Atomic charges with B3LYP
6-31+G(d,p)		6-31+G(d,p)	
C1	0.014256	C14	0.581270
C2	-0.046435	C15	0.083945
C3	0.013151	C16	-0.131725
C4	-0.232924	C17	0.105304
C5	-0.014105	H18	0.088259
C6	-0.056589	C19	0.120104
H7	0.022491	H20	0.016963
H8	0.012234	H21	0.064517
H9	0.060892	Cl22	-0.365581
H10	0.049796	O23	-0.766532
H11	0.028996	N24	-0.825527
C12	1.119068	H25	0.253564
C13	-0.534887	H26	0.339495

Other molecular Properties:

The calculated several thermodynamic parameters have been presented as shown in Table 4. The zero – point vibrational energies (ZPVE), Thermal energy, Molar capacity at constant volume and entropy were calculated by B3LYP/6-31+G (d,p) basis set.

HOMO-LUMO Gap:

Many organic molecules, containing conjugated π electrons are characterized by large values of molecular first hyperpolarizabilities, were analyzed by means by vibrational spectroscopy.

The interaction of two atomic (or) molecule orbital produces two new orbitals. One of the new orbitals is higher in energy than the original ones (the anti bonding orbital) and one is lower (the lower orbital). HOMO, LUMO energy characterizes the ability of electron accepting [9]. When one of the initial orbitals is filled with a pair of electrons (a Lewis base) and the other is empty (a Lewis acid), we can place the two electrons into the lower, energy of the two new orbitals. The

“Filled- Empty” interaction therefore is stabilizing. When we are dealing with interacting molecular orbitals, the two that interact are generally the highest energy occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the compound [10-11]. These orbitals are a pair of orbitals in the compound, which allows them to interact most strongly. These orbitals are sometimes called the frontier orbitals, because they lie at the outermost boundaries of the electrons of compound. The HOMO-LUMO energy gap of 2A5CB was calculated using B3LYP/6-31+ G (d,p) basis set. The HOMO-LUMO gap value of the studied compound is -0.28388 a.u.

Table.4 Theoretically computed zero-point vibrational energy, rotational constant, rotational temperature, vibrational temperature, thermal energy, molar capacity at constant volume and entropy for 2A5CB

Parameters	B3LYP/6-31+G(d,p)
Zero point vibration energy (kcalmol ⁻¹)	126.50077
Rotational constants (GHz)	
A	0.66687
B	0.32446
C	0.22909
Rotational temperature (k)	
A	0.03200
B	0.01557
C	0.01099
Thermal energy (kcalmol ⁻¹)	
Total	134.576
Translational	0.889
Rotational	0.889
Vibrational	132.799
Molar capacity at constant volume (calmol ⁻¹ k)	
Total	50.722
Translational	2.981
Rotational	2.981
Vibrational	44.760
Entropy (calmol ⁻¹ k)	
Total	114.234
Translational	42.214
Rotational	33.139
Vibrational	38.881

The HOMO-LUMO energy gap of 2A5CB, reveals that the energy gap reflects the chemical activity of the molecule. LUMO as an electron acceptor represents the ability to obtain an electron, HOMO represents the ability to donate an electron. Moreover the lower value in the HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule[12].

Nonlinear optical properties:

The Kurtz and Perry [13] technique was needed to investigate its SHG, which was considered as a tool to evaluate the non centrosymmetry nature of the samples. A high intensity Nd:YAG laser with fundamental radiation of 1064nm as the optical source and directed onto the powder sample. SHG efficiency has been estimated as three times greater than that of KDP crystal powder. Its non centro symmetric structure and SHG behavior were confirmed from the output of green light emission from the crystal [14].

CONCLUSION

Atoms have been made to study the structural and vibrational spectra of 2A5BC using DFT calculations. The first order hyperpolarizability of 2A5BC is found to be $3.572400255 \times 10^{-30}$ esu which is nearly eighteen times than that of urea. Furthermore, the thermodynamic, nonlinear optical, first order hyperpolarizability and total dipole moment properties of the compound were also obtained from the optimized structure. HOMO, LUMO orbital localization also confirm the intramolecular charge transfer which can be indicative for having the optical nonlinear property of 2A5CB.

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