



Spectroscopic (FT-IR, FT-Raman) and quantum mechanical studies of 3*t*-pentyl-2*r*,6*c*-diphenylpiperidin-4-one thiosemicarbazone



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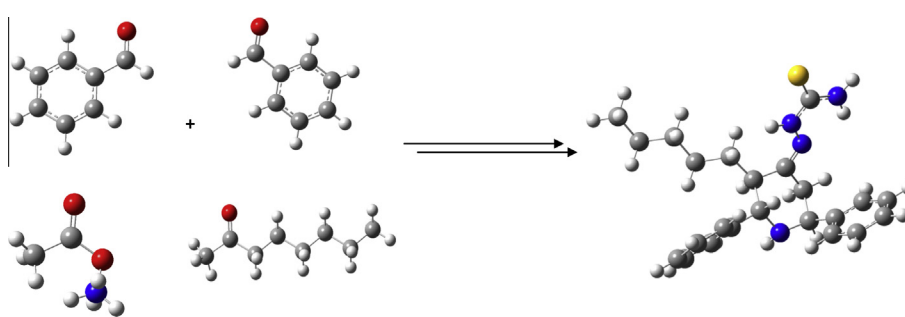
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HIGHLIGHTS

- Mulliken and MEP analyses are used to identify reactive sites in PDPOTSC.
- NBO analysis indicates that the hyperconjugation interaction takes place between LP (1) N52 atom to π^* C3–N51 and π^* C53–S54.
- The small energy gap indicates that charge transfer takes place within the molecule.
- Higher first hyperpolarizabilities value shows that the molecule has good NLO behavior.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the molecular structure and vibrational spectra of 3*t*-pentyl-2*r*,6*c*-diphenylpiperidin-4-one thiosemicarbazone (PDPOTSC) were studied. The ground-state molecular geometry was ascertained by using the density functional theory (DFT)/B3LYP method using 6-31++G(d,p) as a basis set. The vibrational (FT-IR and FT-Raman) spectra of PDPOTSC were computed using DFT/B3LYP and HF methods with 6-31++G(d,p) basis set. The fundamental vibrations were assigned on the basis of the total energy distribution (TED $\geq 10\%$) of the vibrational modes, calculated with scaled quantum mechanics (SQM) methods PQS program. The electrical dipole moment (μ) and first hyperpolarizability (β_o) values have been computed using DFT/B3LYP and HF methods. The calculated result (β_o) shows that the title molecule might have nonlinear optical (NLO) behavior. Atomic charges of C, N, S and molecular electrostatic potential (MEP) were calculated using B3LYP/6-31G++(d,p). The HOMO–LUMO energies were calculated and natural bonding orbital (NBO) analysis has also been carried out.

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Introduction

Piperidone derivatives and thiosemicarbazones were reported to be associated with antitumor, antibacterial, antiviral, antimalarial and antiprotozoal activities [1–4]. The FT-IR and FT-Raman spectra combined with quantum chemical computations have been recently used as an effective tool in the vibrational analysis of drug

molecules [5], biological compounds [6] and natural products [7], since FT-Raman spectra and computed results can help unambiguous identification of the vibrational modes as well as the bonding and structural features of organic molecular systems. Both the IR and Raman spectroscopic analyses have been used to obtain the structural information on molecules.

A literature survey reveals to the best of our knowledge that no *ab initio* HF/DFT wavenumbers and structural parameters calculation of 3*t*-pentyl-2*r*,6*c*-diphenylpiperidin-4-one thiosemicarbazone has been reported so far. In the present study, HF and DFT levels of

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theories were used to determine the optimized geometry, vibrational wavenumbers in its ground state, dipole moment (μ), polarizability (α), hyperpolarizability (β), chemical potential, hardness (η), HOMO–LUMO energies and thermodynamic parameters. Molecular electrostatic potential (MEP) diagram also has been discussed. In addition, NBO analysis of PDPOTSC was performed in the same level of theories to determine the second order perturbation energy in terms of delocalization energy $E^{(2)}$.

Experimental

Synthesis of 3*t*-pentyl-2*r*-,6*c*-diphenylpiperidin-4-one thiosemicarbazone

3*t*-Pentyl-2*r*-,6*c*-diphenylpiperidin-4-one thiosemicarbazone was prepared according to procedure described by literature method [8].

FT-IR and Raman spectra

The FT-IR spectrum of the synthesized title compound was measured in accumulated scan 64 with 4 cm^{-1} resolution, $4000\text{--}400\text{ cm}^{-1}$ range on a AVATAR-330 FT-IR spectrometer (Thermo Nicolet) using KBr (pellet form). The FT-Raman spectrum of PDPOTSC has been recorded using 1064 nm line Nd:YAG laser as excitation wavelength in the region $100\text{--}4000\text{ cm}^{-1}$ on a Thermo Electron corporation model Nexus 670 spectrophotometer equipped with FT-Raman module accessory and the FT-Raman spectrum was recorded at Central Electro Chemical Research Institute, Karaikudi, Tamilnadu.

Quantum chemical calculations

Electronic structure calculations have been performed at DFT (B3LYP) and HF methods with 6-31++G(d,p) basis set using the Gaussian 03W [9] program package, invoking gradient geometry optimization [10,11]. The structures of the conformers were obtained by performing geometry optimization, without imposing any symmetry constraints. Vibrational frequency calculations were carried out on the optimized geometries. HF and DFT hybrid B3LYP functional methods tend to overestimate the fundamental modes. Therefore, scale factor has to be used for obtaining a considerably better agreement with experimental data [12]. Thus, the scale factors 0.9608 and 0.8992 have been uniformly applied to the DFT/B3LYP and HF methods, respectively. NBO analysis has been performed on PDPOTSC by using B3LYP/6-31++G(d,p) level theory in order to elucidate the role of delocalization interactions.

Prediction of Raman intensity

It should be noted that Gaussian 03 package does not calculate the Raman intensities. The Raman activities were transformed into Raman intensities using Raint program [13] by the expression:

$$I_i = 10^{-12} \times (v_0 - v_i)^4 \times \frac{1}{v_i} \times RA_i$$

where I_i is the Raman intensity, RA_i is the Raman scattering activities, v_i is the normal modes and v_0 denotes the wavenumber of the excitation laser [14].

Results and discussion

Conformation analysis and geometry optimization

Major experimental and computational efforts are being devoted to determine and interpret even subtle variations in structural substituent effects originating from conformational changes [15–17]. Conformational analysis of the PDPOTSC was carried out using G03 program. The possible geometry of the conformers was optimized to find out the energetically and thermodynamically most stable configuration of the compound and it is shown in Fig. S1. The stability of the stable conformer is in the order $1 > 4 > 3 > 2$. The corresponding energy, energy difference and dipole moment are presented in Table 1. From Table 1, we conclude that 1 is stable conformer and take conformer 1 for further studies.

The optimized bond lengths, bond and dihedral angles of PDPOTSC calculated by B3LYP and HF methods with 6-31++G(d,p) basis set are listed in Table 2, in accordance with atom numbering scheme as shown in Fig. 1. Since, the crystal structure data of the title compound is not available till now, the optimized geometrical parameters are compared with other similar system 3-methyl-2,6-bis(4-chlorophenyl) piperidin-4-one thiosemicarbazone [18] for which experimental crystal data have been obtained. It is seen that the various bond lengths are found to be greater than the experimental values. This over estimation can be explained on the basis that the theoretical calculation belongs to isolated molecule in gas phase while the experimental results belong to molecule in solid state.

The calculated C–C bond distances in the heterocyclic ring is in the range 1.585–1.508 and 1.554–1.512 Å by B3LYP and HF methods, respectively, which compared favourably with experimental values (1.535–1.499 Å) [18] and are listed in Table 2. The optimized bond lengths of C–C in phenyl ring fall in the range 1.403–1.394 and 1.519–1.383 Å for B3LYP and HF, respectively. These values are in agreement with literature values [18]. The calculated value is around 0.98–1.086 Å and reported value is 0.97 Å [18]. This deviation is due to XRD having recorded in solid phase, whereas computational study in gas phase. For the title compound, the C–N bond lengths in the range 1.471–1.288 and 1.449–1.257 Å by B3LYP and HF methods, respectively, which are in agreement with the reported values 1.460–1.288 Å [18]. The optimized N–H bond lengths fall in the range 1.000–0.993 Å by B3LYP and HF methods with 6-31++G(d,p) basis set, respectively. By comparing these values with experimental value 0.860 Å [18], it is predicted that HF estimate for N–H bond length is better than B3LYP method. The bond lengths of thiosemicarbazone moiety show variations from their normal values and this may be due to the delocalization of π electron density, which results in the partial double bond character in thiosemicarbazone moiety [N51–N52 = 1.365,

Table 1
Calculated energies and energy differences of possible conformers of the PDPOTSC by DFT (B3LYP/6-31++G(d, p)) method.

Conformer	Energy		Energy differences		Dipole moment (Debye)
	(Hartree)	(kcal/mol)	(Hartree)	(kcal/mol)	
Conformer-1	–1511.7478	–948636.11	0	0.00	6.23
Conformer-2	–1511.72323	–948620.69	0.0246	15.4179	5.21
Conformer-3	–1511.73971	–948631.03	0.0081	5.0766	4.90
Conformer-4	–1511.74323	–948633.24	0.0046	2.8677	5.13

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