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INVESTIGATION OF ELECTRONIC AND MOLECULAR PROPERTIES OF 5-(3-METHYL-3-PHENYLCYCLOBUTYL)-N-PHENYL-3,6-DIHYDRO-2H-1,3,4-THIADIAZIN-2-IMINE BY EXPERIMENTAL AND THEORETICAL METHODS

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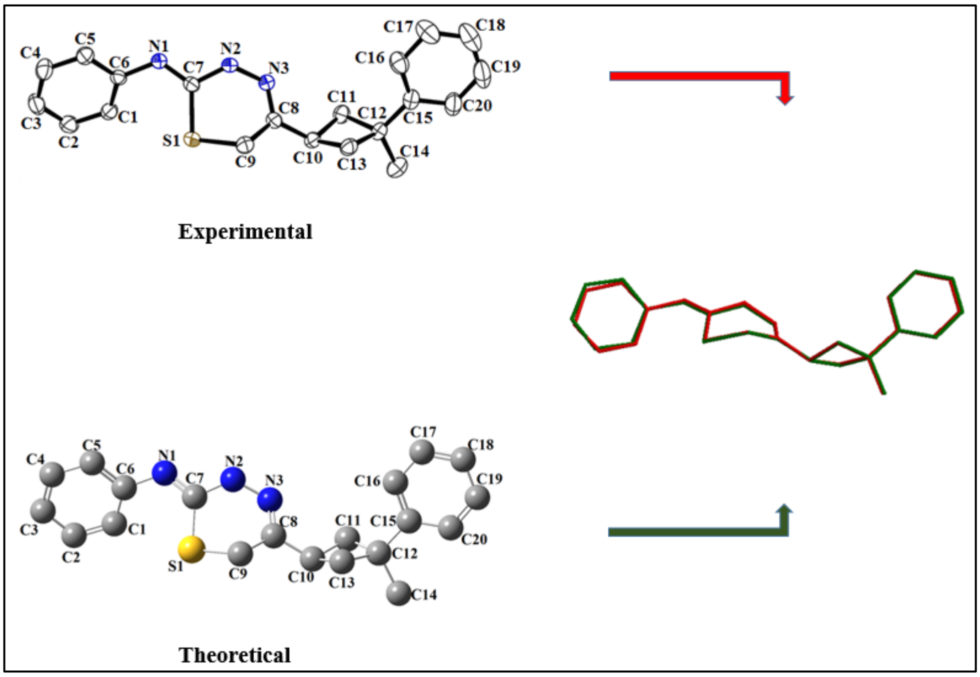
ABSTRACT

In this work, 5-(3-methyl-3-phenylcyclobutyl)-N-phenyl-3,6-dihydro-2H-1,3,4-thiadiazin-2-imine ($C_{20}H_{21}N_3S$), MPDT, was prepared and characterized by X – ray single crystal diffraction and IR and ^{13}C-NMR spectroscopic techniques. The molecular geometry, vibrational frequencies, gauge including atomic orbital (GIAO) ^{13}C chemical shift values of MPDT in the ground state have been calculated by using the Hartree-Fock (HF) and Density Functional Theory (B3LYP) with 6-31G(d) basis set. The scaled B3LYP/6-31G(d) results shows the best agreement with the experimental values over the other method. B3LYP is applied to explore the Mulliken atomic charges of the title molecule. In addition to frontier molecular orbital (FMO) and molecular electrostatic potential (MEP) of the title molecule have been calculated by using the HF and B3LYP with 6-31G(d) basis set.

Keywords: Cyclobutane, X-ray structure determination, IR and (^{13}C) NMR spectroscopy, Hartree-Fock (HF) Density Functional Theory (DFT).

GRAPHICAL ABSTRACT



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5-(3-METHYL-3-PHENYLCYCLOBUTYL)-N-PHENYL-3,6-DİHYDRO-2H-1,3,4-THİADİAZİN-2-İMİNENİN DENEYSEL VE TEORİK METOTLARLA MOLEKÜLER VE ELEKTRONİK ÖZELLİKLERİNİN İNCELENMESİ

ÖZET

Bu çalışmada, 5-(3-methyl-3-phenylcyclobutyl)-N-phenyl-3,6-dihydro-2H-1,3,4-thiadiazin-2-imine ($C_{20}H_{21}N_3S$), MPDT, IR ve ^{13}C-NMR spektroskopik teknikleriyle ve X-ışını tek kristal kırınımı ile karakterize edilip hazırlandı. Temel halde molekülün, moleküler geometri, titreşim frekansları, GIAO ^{13}C kimyasal değişim değerleri 6-31G(d) baz seti ile HF ve B3LYP metotları kullanılarak hesaplandı. B3LYP/6-31G(d) de elde edilen sonuçları diğer metoda kıyasla deneysel veriler ile daha uyumlu sonuçlar gösterdi. Bu sebeple molekülün Mulliken yük dağılımları B3LYP ile hesaplandı. Ek olarak molekülün moleküler orbital ve moleküler elektrostatik potensiyeli de HF/6-31G(d) ve B3LYP/6-31G(d) kullanılarak hesaplandı.

Anahtar Kelimeler: Siklobütan, X-ışını ile yapı belirleme, IR ve (^{13}C) NMR spektroskopisi, Hartree-Fock (HF), Yoğunluk Fonksiyoneli Teorisi (DFT)

1. INTRODUCTION

5-(3-methyl-3-phenylcyclobutyl)-N-phenyl-3,6-dihydro-2H-1,3,4-thiadiazin-2-imine is a novel compound firstly prepared in our laboratories by us so there is no information about it in the literature. In order to support the experimental data, various computational techniques have been developed all over the world. Nowadays structural and electronic properties of atoms, molecules and solids can be calculated with great accuracy with the Density Functional Theory. The electronic structure and spectroscopic assignments of a molecule with given molecular geometry, have been calculated with following methods. DFT provides a variety of methods such as LSDA, BPV86, and B3LYP. B3LYP stands for Becke 3-Parameter (Exchange), Lee, Yang and Parr (Correlation; density functional theory) [1, 2].

In this paper, MPDT was described and characterized by 13C-NMR, IR and single-crystal X-ray diffraction methods as well as theoretical studies in the ground state which have been calculated using the HF and B3LYP with 6-31G(d) basis set.

2. MATERIALS AND METHODS

2.1. Synthesis

To a stirred solution of 4-phenyl thiosemicarbazide (1.6723 g, 10 mmoL) in 20 mL absolute ethanol, a solution of 2-chloro-1-(3-methyl-3-phenylcyclobutyl)ethanone (2.2271 g, 10 mmoL) in 10 mL absolute ethanol was added at 0 ºC and stirred for additional fifteen minutes (TLC). Light yellow precipitate separated by suction, washed with copious water and crystallized from acetone. Yield: 95%, melting point: 438 K. (see Figure 1).

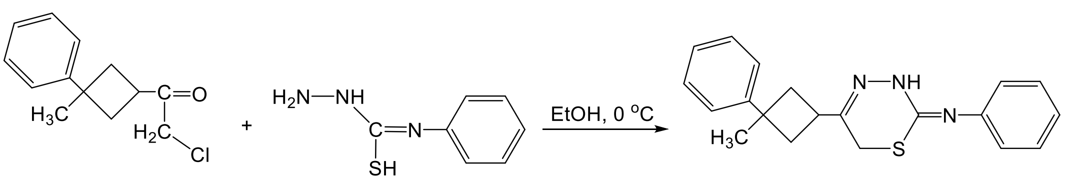

Figure 1. Synthetic pathway for the synthesis of the target compound

2.2. General Remarks

All chemicals were of reagent grade and used as in commercially available forms without further purification. Melting point was determined by Gallenkamp melting point apparatus. The IR spectra of the compound were recorded in the range of 4000–400 cm^{-1} using a Mattson 1000 FT-IR spectrometer with KBr pellets. The ^{13}C-NMR spectra were recorded on a Varian-Mercury-Plus 400 MHz spectrometer using TMS as internal standard and $CDCl_3$ (chloroform) as solvent.

2.3. Crystallography

All diffraction measurements were performed at room temperature (293 K) using graphite monochromatic MoKα radiation (k = 0.71073 Å) radiation and STOE IPDS (II) diffractometer. A suitable sample with the size of 0.62 × 0.42 × 0.13 mm was selected for the crystallographic study. Reflection data was recorded in the rotation mode using the ω scan technique by using X-AREA software [3]. Intensity parameters were collected in the θ range $2.7^\circ \leq \theta \leq 27.1^\circ$. The structure was solved by direct methods using SHELXS-97 [4] implemented in the WinGX [5] program suite. The refinement was carried out by full-matrix least-squares method on the positional and anisotropic temperature parameters of the non-hydrogen atoms, or equivalently corresponding to 222 crystallographic parameters, using SHELXL-97 [6]. Computing data collection: X-AREA, cell refinement: X-AREA, computing data reduction: X-RED. The general-purpose crystallographic tool PLATON [7] was used for the structure analysis and presentation of the results. The structure was refined to R_{int} = 0.085 with 1689 observed reflections using $I > 2\sigma(I)$ threshold. The molecular graphic were displayed using ORTEP-3 for Windows [8]. Details of the data collection conditions and the parameters of the refinement process are given in Table 1.

Table 1. Crystal data and structure refinement parameters for the title compound

CCDC deposition no.	1061682
Chemical formula	$C_{20}H_{21}N_3S$
Formula weight	335.46
Temperature (K)	293(2)
Wavelength (A˚)	0.71073 Mo Kα
Crystal system	Orthorhombic
Shape	Plate
Space group	P b c a
Unit cell parameters	
a,b,c (A˚)	8.8028(5), 12.8690(7), 31.1611(16)
α,β,γ (˚)	90.00
Volume $A^{\circ 3}$	3530.0(3)
Z	8
Calculated density (Mg/m^3)	1.262
μ (mm^{-1})	0.189
F_{000}	1424
Crystal size (mm)	0.62 × 0.42 × 0.13
h_{min}, h_{max}	-11, 10
k_{min}, k_{max}	-16, 16
l_{min}, l_{max}	-39, 30
Theta range for data collection (˚)	$2.7 \leq \theta \leq 27.1$
Measured reflections	15198
Independent reflections	3867
Refinement method	Full-matrix least-squares on F^2
$wR(F^2)$	0.066
$R[F^2 > 2\sigma(F^2)]$	0.039
R_{int}	0.085
$\Delta\rho_{max}$, $\Delta\rho_{min}$ ($e/A^{\circ 3}$)	0.15, −0.16

2.4. Quantum Chemical Calculations

All the calculations were performed without specifying any symmetry for the title molecule by using Gauss View molecular visualization program [8] and Gaussian 03 program package [9]. For modeling, the initial guess of the compound was first obtained from the X-ray coordinates and the structure was optimized by Hartree–Fock (HF) and Density Functional Theory (DFT)/B3LYP methods [10, 1] with the 6-31G(d) basis set. ^{13}C-NMR chemical shift are calculated within GIAO approach [11, 12] applying HF and B3LYP method with 6-31G(d) basis set. In addition to frontier molecular orbitals and molecular electrostatic potential map analysis were investigated by theoretical calculations

3. RESULTS AND DISCUSSION

3.1. Geometrical Structure

An ORTEP view of the title compound and the B3LYP optimized structure of the title compound are shown in Figure 2, where the compound crystallizes in the orthorhombic space group Pbca with eight molecules in the unit cell (Z = 8). The unit cell dimensions are a = 8.8028(5) Å, b = 12.8690(7) Å, c = 31.1611(16) Å and V = 3530.0(3) Å^3. The title molecule is composed of a cyclobutane ring and two benzene rings.

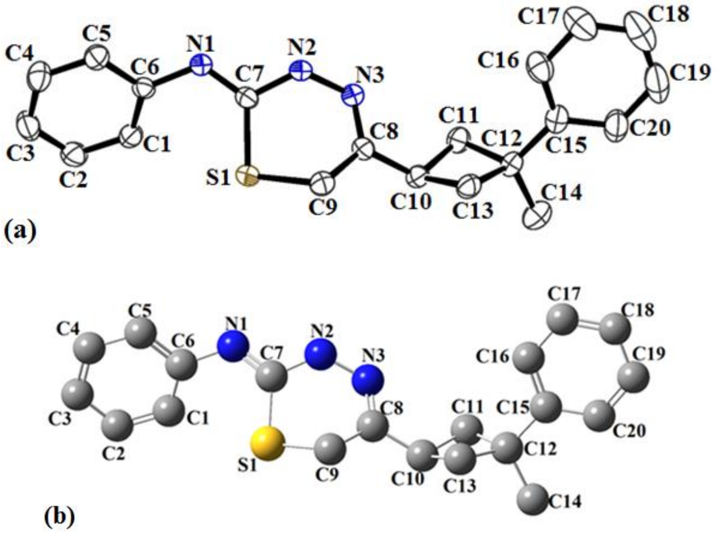

Figure 2. (a) A view of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. (b) The theoretical geometric structure of the title compound (B3LYP/6-31 G(d) level)

The crystal structure could be described as being built from essentially planar fragments, the aromatic ring **A** (C1—C6), N1 atom is linking **B** (C7—S1), the cyclobutane plane **C** (C10—C13) and the other aromatic ring **D** (C15—C20). The dihedral angles between **A**, **B**, **C** and **D** are 50.16(0.08)˚ **(A/B)**, 48.88(0.08)˚ **(B/C)**, 87.82(0.08)˚ **(C/D)**.

It is well known that 3-substituted cyclobutane carboxylic acid derivatives exhibit anti-inflammatory and antidepressant activities [13] as well as liquid crystal properties [14]. The popular anticancer drug, carboplatin, also contains a cyclobutane ring [15]. Cyclobutane ring has adopted a puckered conformation and although the value for the puckering of the cyclobutane ring found in the literature is 19.8(3)˚ [16], there is a negligible puckering in the cyclobutane ring (torsion angles; C12—C11—C10—C13 and C10—C13—C12—C11; 15.07(15)˚ and 14.90(16)˚, respectively). When the bond lengths and angles of the cyclobutane ring in the title molecule are compared with the previously reported cyclobutane derivatives [17-20], it is seen that there are no significant differences.

Perspective view of the crystal packing in the unit cell is shown in Figure 3. In the crystal packing, there is a C—H•••S hydrogen bonding, and the details of which are given in Table 2. The crystal structure of MPDT shows an intramolecular bond-interaction. In this hydrogen bonding, atom S1 acts as a donor to related C1 at (2-x,-y,-z).

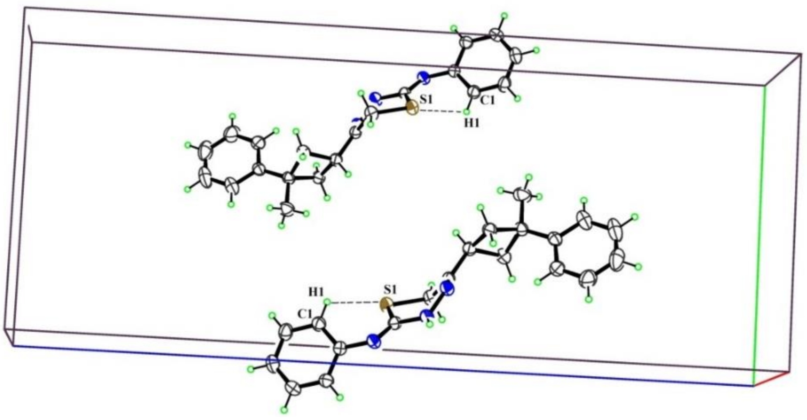

Figure 3. Part of the crystal structure of the title compound, showing the C1–H1···S1 interactions

Table 2. Hydrogen bond geometries in crystal structure (Å, ˚)

D—H···A	D—H	H···A	D···A	D—H···A
C1–H1···S1	0.93	2.60	3.045 (2)	110

Symmetry codes: 2-x,-y,-z.

3.2. Optimized Structures

The optimized parameters (bond lengths, bond angles and torsion angles) of the title compound have been obtained using HF and B3LYP methods with the 6-31G(d) basis set. Some selected geometrical parameters which have been experimentally gathered and theoretically calculated are listed in Table 3. From Table 3, it can be seen that there are some deviations in the computed geometrical parameters from those data, and these differences are probably due to the intramolecular interaction.

Table 3. Some selected experimental and optimized geometrical parameters of the title compound

Geometric parameters	Experimental (X-ray)	Calculated [6-31G(d)]	
		HF	B3LYP
Bond lengths (A˚)			
C1-C6	1.386(3)	1.3897	1.4062
C6-N1	1.408(3)	1.4078	1.4006
S1-C7	1.759(2)	1.7757	1.7933
N2-N3	1.396(2)	1.3854	1.3859
C8-C10	1.489(3)	1.5007	1.5002
C10-C11	1.534(3)	1.5396	1.5469
C11-C12	1.543(3)	1.5592	1.5708
C12-C14	1.530(3)	1.5307	1.5332
C15-C16	1.379(3)	1.3972	1.4066
R^2		0.9953	0.9889
Bond angles (˚)			
C2—C3—C4	119.5(2)	119.3454	119.3759
C5—C6—N1	117.96(18)	119.3491	117.949
N1—C7—S1	126.66(17)	125.8496	127.0803
C7—N2—N3	125.02(18)	122.8985	126.0701
N2—N3—C8	116.56(18)	117.4256	117.2056
C8—C10—C13	116.50(17)	116.9861	117.2379
C10—C11—C12	90.13(16)	89.7584	90.072
C14—C12—C15	113.63(19)	113.4319	113.677
R^2		0.9908	0.9989
Torsion angles (˚)			
C1—C2—C3—C4	0.8(4)	0.3333	0.7463
C5—C6—N1—C7	143.0(2)	108.6945	133.419
N1—C6—C5—C4	176.7(2)	177.63	178.62
C10—C11—C12—C14	95.96(19)	95.5586	96.0979
R^2		0.9499	0.9954

We have displayed the correlation graph in Figure 4 based on the correlation calculations. The correlation values (R^2) have been found as 0.9953 and 0.9889 for bond lengths, 0.9908 and 0.9989 for bond angles, 0.9499 and 0.9954 for torsion angles at HF/6-31G(d) and B3LYP/6-31G(d) levels, respectively. According to correlations values, the B3LYP/6-31G(d) method gave accurate results for the bond angles, when torsion angles compared with the HF/6-31G(d) method.

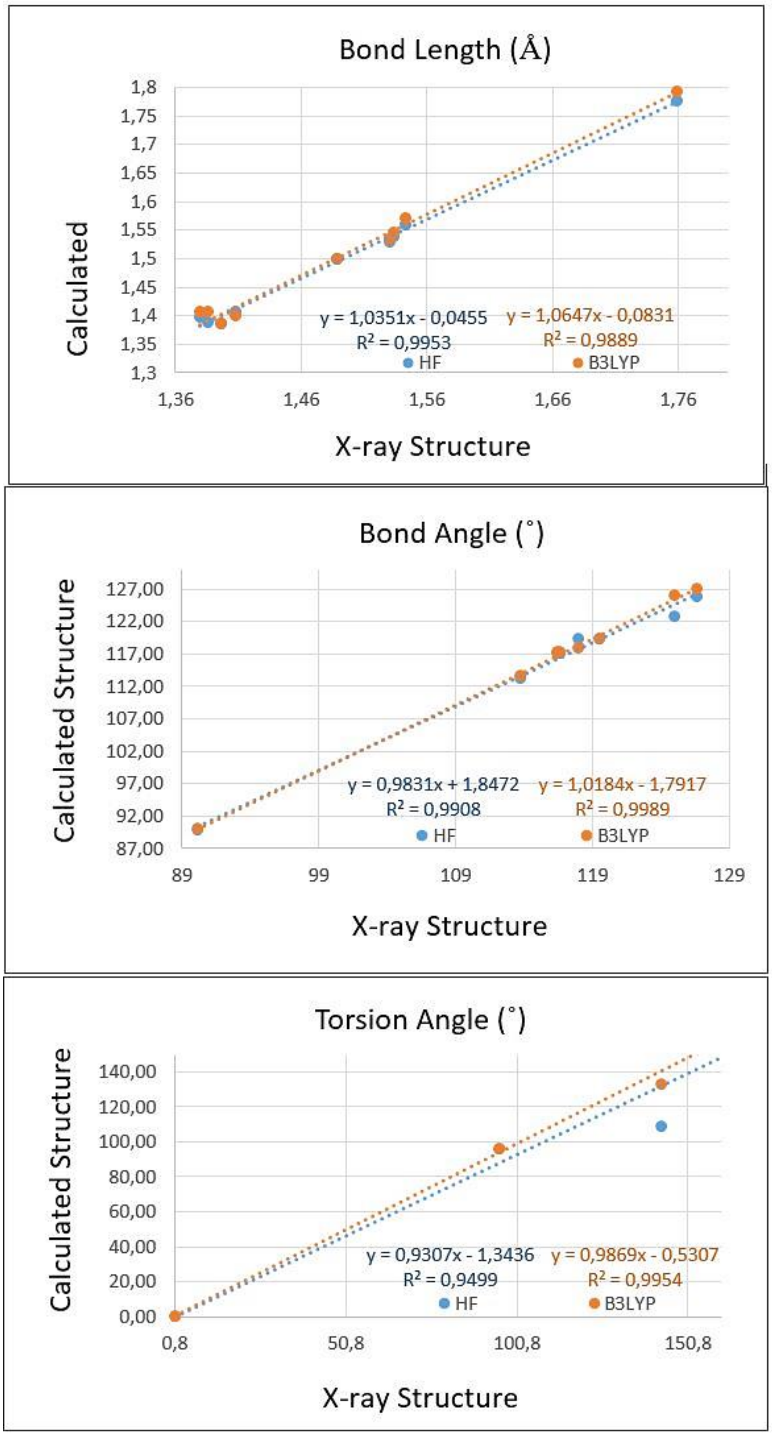

Figure 4. Correlation graphics between the experimental and theoretical geometric parameters of the title compound

A global comparison was performed by superimposing the molecular skeletons obtained from the X-ray diffraction and the theoretical calculations atom by atom (Figure 5), obtaining RMSE values of 0.232 and 0.107 Å for HF/6-31G(d) and B3LYP/6-31G(d), respectively. According to these results, the smallest RMSE value is acquired for B3LYP/6-31G(d) and the geometry obtained from this method coincides better with the crystalline structure than HF/6-31G(d) method. For that reason, we used the geometry from B3LYP/6-31G(d) method, to calculate molecular electrostatic potential (MEP) and frontier molecular orbitals (FMOs).

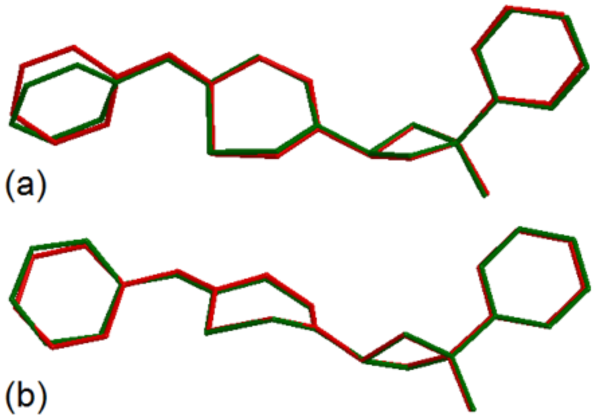

Figure 5. Atom-by atom superimposition of the calculated structures calculated (green) (a = HF/6-31 G(d), b = B3LYP/6-31 G(d)) on the X-ray structure (red) of the title compound

3.3. IR Spectroscopy

The experimental IR spectra of the title compound are shown in Figure 6. The vibrational bands have been assigned using GaussView molecular visualization program and calculated bands with both HF and B3LYP approach along with selected experimental counterparts which are indicated in Table 4.

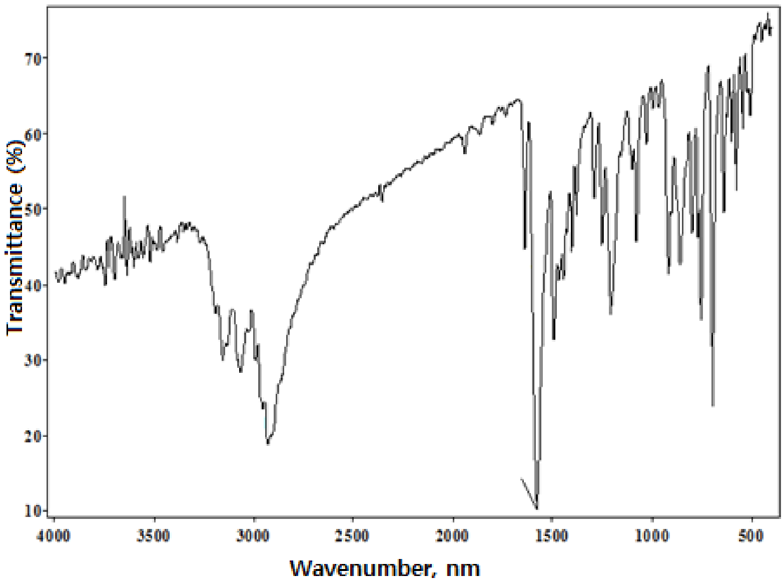

Figure 6. Experimental IR spectra of the title compound

Table 4. Comparisons of the observed and calculated vibrational spectra of the title compound

Assignment	**Experimental**	**Calculated [6-31 G(d)]**	
	FT-IR (cm^{-1})	**HF**	**B3LYP**
ν_sN–H	3259	3584	3477
ν_{as}C–H$_{aromatic}$	3067	3026	2868
ν_{as}C–H$_{2cyclobutane}$	2961	3036	3015
νC–H$_{cyclobutane}$	2855	2861	2834
$\Theta_{cyclobutane}$	1036	946	918
R^2		0.9835	0.9784

Vibrational modes ν, stretching; s, symmetric; as, asymmetric; Θ,ring breathing.

Aromatic C—H vibrations

The C—H asymmetric stretching vibrations are observed at 3105 cm^{-1} in FT-IR spectrum [21]. In the title compound, the C—H asymmetric stretching vibration is observed at 3067 cm^{-1}, which has been calculated at 3026 cm^{-1} for HF level, 2868 cm^{-1} for B3LYP level. There are no peaks observed in FT-IR spectrum for C—H symmetric stretching vibrations.

N—H vibrations

The N—H aromatic stretching vibrations were occurred at 3300-3500 cm^{-1} [22]. In previous study, N—H stretching vibration was founded at 3330-3481 cm^{-1} [23]. In here, the N—H stretching vibration is observed at 3259 cm^{-1} as a very strong band in FT-IR spectrum and its corresponding calculated frequencies are 3584 and 3477 cm^{-1} using HF/6-31G(d) and B3LYP/6-31G(d), respectively.

Cyclobutane vibrations

In the title molecule, there are many cyclobutane ring vibrations. The asymmetric stretching of C—H$_2$ was observed at 2939 and 2855 cm^{-1} [24]. The symmetric and asymmetric stretching are observed at 2855 and 2961 cm^{-1} in FT-IR spectrum. These modes have been calculated at 2861, 2834 cm^{-1} with HF/6-31G(d) and 3036, 3015 cm^{-1} with B3LYP/6-31G(d), respectively.

The correlation values (R^2) have been found as 0.9835 and 0.9784 for HF/6-31G(d) and B3LYP/6-31G(d), respectively. According to the correlations values, the B3LYP/6-31G(d) method gave accurate results for the vibration modes compared with the HF/6-31G(d) method.

3.4. NMR Spectra

The isotropic chemical shifts are frequently used as an aid in identification of organic compounds and accurate predictions of molecular geometries that are essential for reliable studies of magnetic properties [25]. The experimental ^{13}C-NMR spectra of the title compound recorded using TMS as an internal standard and chloroform ($CDCl_3$) as solvent are shown in Figure 7. The theoretical ^{13}C chemical shifts are calculated for the optimized geometry obtained from HF/6-31G(d) and B3LYP/6-31G(d) by using Gaussian program with the standard GIAO approach.

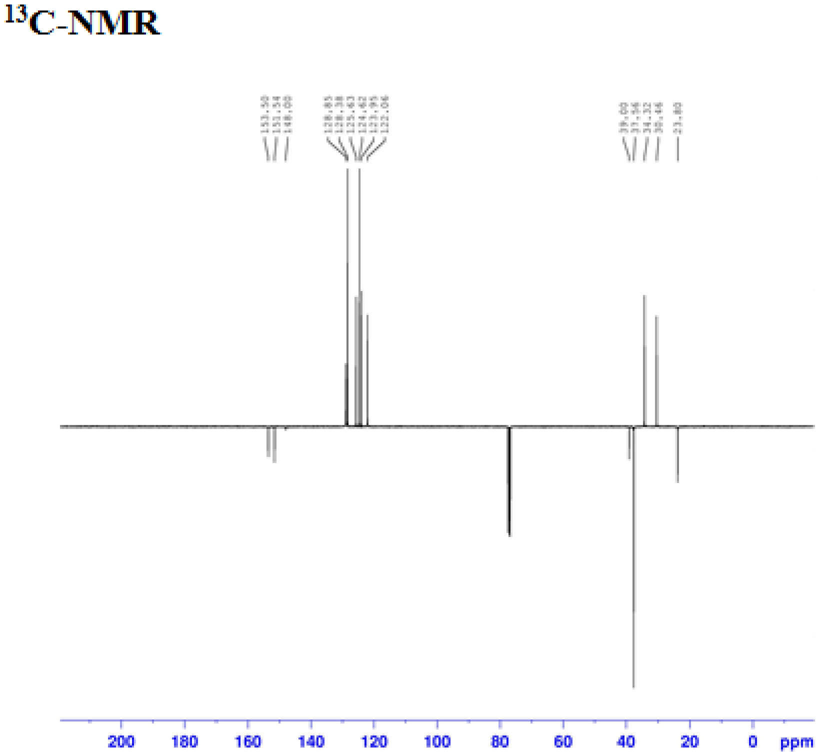

Figure 7. Experimental ^{13}C chemical shift spectra of the title compound

In the experimental ^{13}C-NMR spectrum of MPDT, the signals at 153.6 and 23.79 ppm are assigned to the atoms C8 and C9, respectively. In the cyclobutane ring the ^{13}C-NMR signals of C12 and C13 carbons are at 44.21 ppm [26]. In the present work, the experimental results are attained at 37.52 ppm. The other calculated chemical shifts values can be seen in Table 5.

Table 5. The experimental and calculated ^{13}C isotropic chemical shifts (with respect to TMS, all values in ppm) for title compound

Atom	Experimental (ppm) $CDCl_3$	Calculated/6-31G(d) (ppm)	
		HF	B3LYP
C1	122.02	113.42	118.03
C2	128.88	119.97	122.92
C3	125.64	113.26	117.59
C4	128.88	121.72	124.29
C5	122.02	118.16	121.72
C6	151.54	145.51	151.13
C8	153.6	162.99	159.93
C9	23.79	12.77	25.99
C10	34.31	17.68	32.29
C11	37.52	20.79	33.15
C12	38.99	22.74	40.97
C13	37.52	23.74	37.93
C14	30.46	3.42	12.55
C15	148	144.14	149.95
C16	124	120.42	123.64
C17	128.38	120.36	123.66
C18	124.61	116.15	119.86
C19	128.38	119.27	122.61
C20	124	116.52	120.28
		0.9922	0.9892

The large difference between the experimental and calculated values of the cyclobutane ring may be due to the fact that theoretical calculations of the title molecule have been done in gaseous phase.

In order to compare the chemical shifts, correlation graph between the observed and calculated ^{13}C-NMR chemical shifts is shown in Figure 8. Therefore, the experimentally obtained values are in good agreement with the theoretically computed values by HF/6-31G(d) method when compared to B3LYP/6-31(G) method.

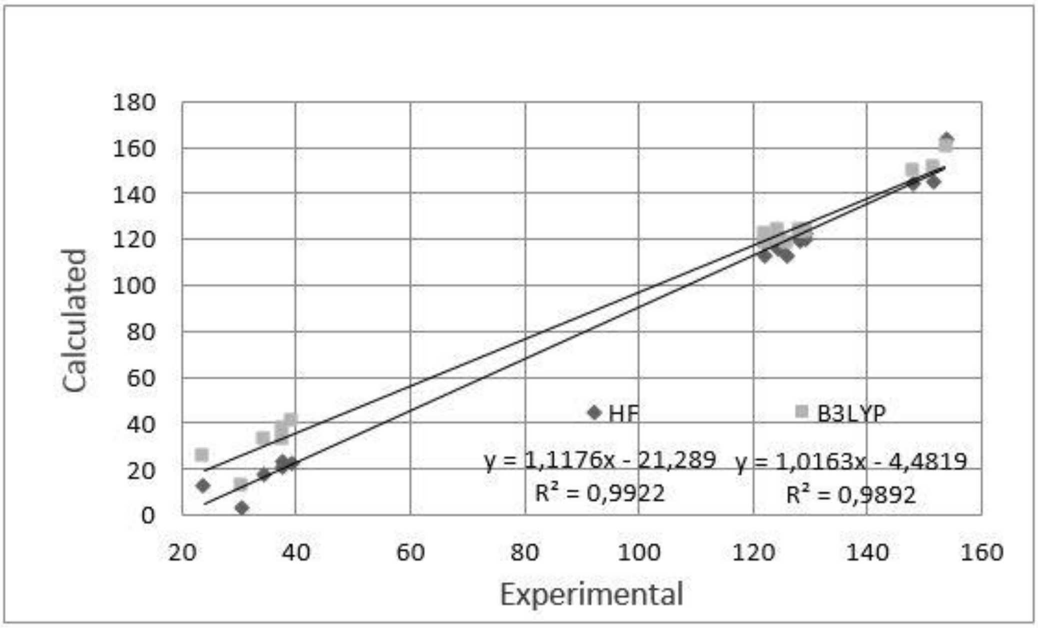

Figure 8. Correlation graphics between the experimental and theoretical NMR chemical shift values of the title compound

Quantum-Chemical Studies

3.5. Molecular Eectrostatic Potential (MEP)

The molecular electrostatic potential (MEP) is related to the electronic density and is a very useful descriptor in understanding sites of electrophilic attack and nucleophilic reactions as well as hydrogen bonding interactions [27, 28]. It is very useful to study the relationship between molecular structures with its physiochemical property.

Different values of electrostatic potential at the surface are represented by different colors. The color scheme for the MEP surface is red-electron rich, partially negative charge (electrophilic reactive centre); blue-electron deficient, partially positive charge; light blue-slightly electron deficient region (nucleophilic reactive centre); yellow-slightly electron rich region; green-neutral, respectively [29]. In the present study, MEP maps of MPDT has been found by HF/6-31G(d) and B3LYP/6-31G(d) methods and shown in Figure 9. The color code of these maps is in the range between -4.834 a.u. to 4.834 a.u. for HF/6-31G(d) and -4.043 a.u. to 4.043 a.u. for B3LYP/6-31G(d).

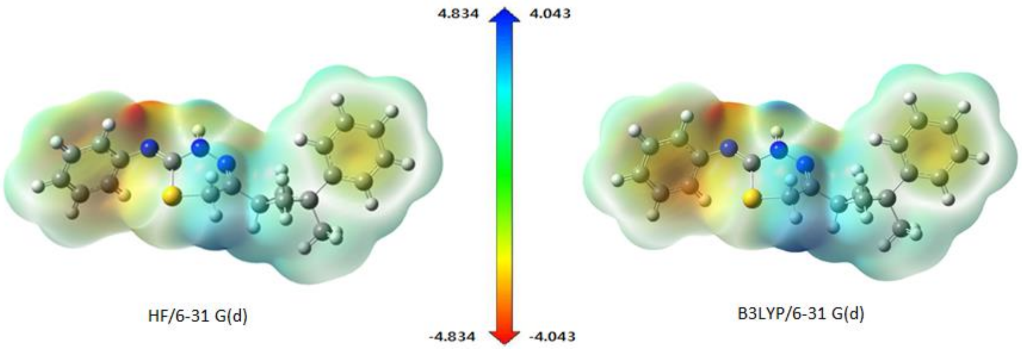

Figure 9. Molecular electrostatic potential map (MEP) (in a.u.) calculated at B3LYP/6-31 G(d) level

Areas of low potential (red) are characterized by an abundance of electrons. Areas of high potential (blue) are characterized by a relative absence of electrons. The region around the nitrogen atom (N1) linked with carbon (C7) through double bond represents the most negative potential region in MPDT. Nitrogen has a higher electronegativity value which would consequently have a higher electron density around them. Thus the spherical region that corresponds to nitrogen atom would have a red portion on it. The MPDT of the compound clearly indicates the electron rich centers of nitrogen atom.

3.6. Frontier Molecular Orbital Analysis (FMO)

The most important frontier molecular orbital (FMO) such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) plays a crucial part in the chemical stability of the molecule [30]. The HOMO represents the ability to donate an electron and LUMO represents the ability of accept an electron [31]. The energy gap between HOMO and LUMO also determines the chemical reactivity, optical polarizability and chemical hardness-softness of a molecule [30]. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule [32]. By examining the frontier orbitals of a molecule the optical properties and the steps to react with other molecules can be determined. The calculations indicate that the title compound has 89 occupied molecular orbitals. The plots of highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are shown in Figure 10.

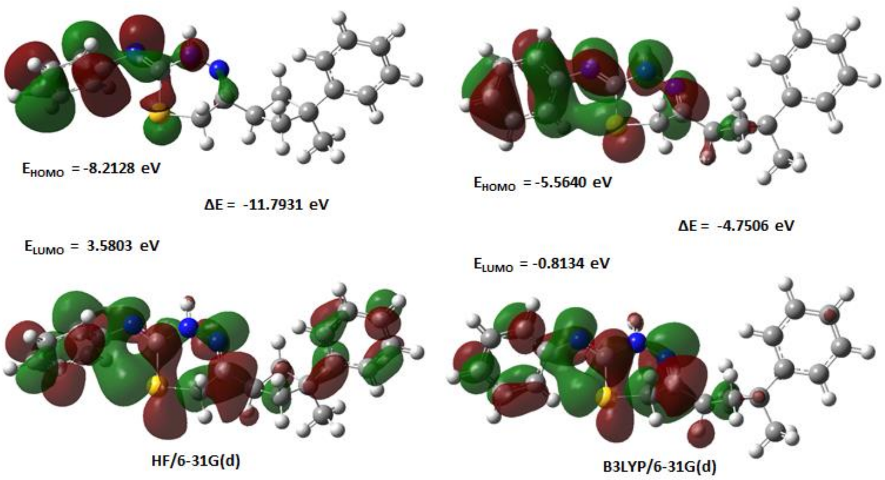

Figure 10. Molecular orbital surfaces and energy levels given for the HOMO and LUMO of the title compound

By using HOMO and LUMO energy values for a molecule, the global chemical reactivity descriptors of molecules such as hardness (η), chemical potential (μ), softness (*S*), electronegativity (χ) and electrophilicity index (ω) have been defined [33, 34]. On the basis of E_{HOMO} and E_{LUMO}, these are calculated using the below equations. Using Koopman's theorem [35] for closed-shell molecules,
The hardness of the molecule is $\eta = (I - A) / 2$,
The chemical potential of the molecule is $\mu = -(I + A) / 2$,
The electronegativity of the molecule is $\chi = (I + A) / 2$,
The electrophilicity index of the molecule is $\omega = \mu^2 / 2\eta$.
Where *A* is the ionization potential and *I* is the electron affinity of the molecule. *I* and *A* can be expressed through HOMO and LUMO orbital energies as $I = -E_{HOMO}$ and $A = -E_{LUMO}$. The calculated values of the hardness, chemical potential, electronegativity and electrophilicity index of our molecule in gas phase are given in Table 6.

Table 6. The calculated values of the title molecule using both HF/ 6-31G(d) and B3LYP/ 6-31G(d) levels

	HF/ 6-31G(d)	B3LYP/ 6-31G(d)
E_{HOMO} (eV)	-8.2128	-5.5640
E_{LUMO} (eV)	3.5803	-0.8134
I (eV)	8.2128	5.5640
A (eV)	-3.5803	0.8134
η (eV)	5.8965	2.3753
μ (eV)	-2.3163	-3.1887
χ (eV)	2.3163	3.1887
ω (eV)	0.4549	2.1403

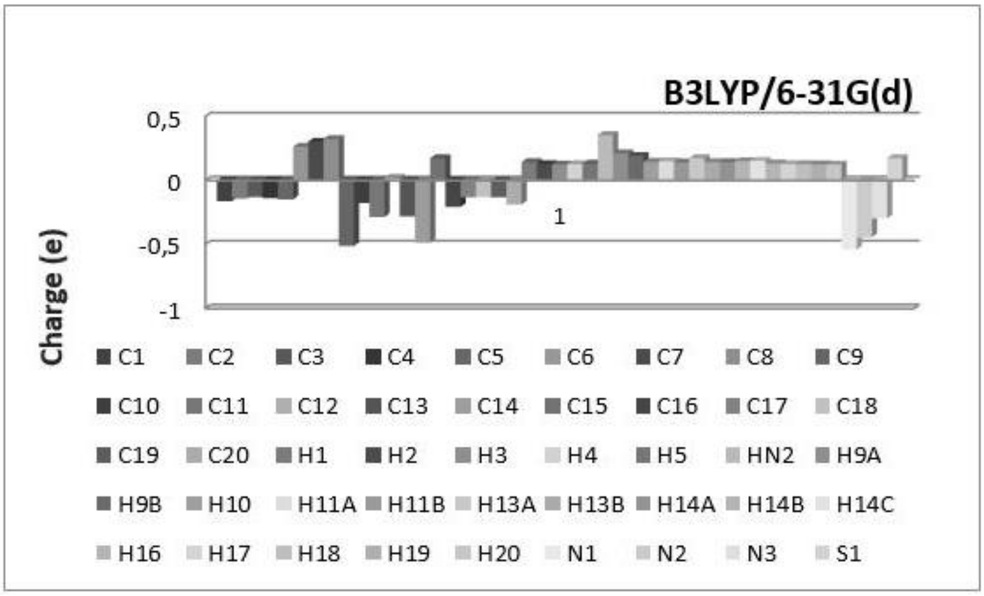

Figure 11. The charge distribution calculated by the Mulliken method for the title molecule

4. CONCLUSIONS

Crystal structure of MPDT was determined and its geometry was optimized by HF and B3LYP method with 6-31G(d) basis set. Theoretical IR and NMR spectroscopies for optimized molecular structure were calculated. Compared to the theoretical and experimental results, compatible results have been observed. Investigations by B3LYP/6-31G(d) level for both the bond angles and torsion angles are performed better. Mulliken atomic charge values are also calculated using same method with basis set. Besides of these properties of the molecule, we have calculated MEP, HOMO-LUMO, hardness, chemical potential, electronegativity and electrophilicity index of the molecule with HF and B3LYP.

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SUPPLEMENTARY DATA

CCDC-1061682 contains the supplementary crystallographic data for the compound reported in this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

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