STRUCTURAL FEATURES OF 2-(4,5-DIPHENYL-4H-1,2,4-TRIAZOL-3-YL)THIO)-1-(3-METHYL-3-PHENYLCYCLOBUTYL)ETHANONE : X-RAY DIFFRACTION AND DFT CALCULATIONS

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ABSTRACT

This paper reported that the combined X-ray diffraction and DFT computational study on molecular structure of the title compound, [C₂₇H₂₅N₃O₂S]. The compound contains a cyclobutane, a triazole and three phenyl rings. The molecular geometry of the compound was brought to light by X-ray single crystal structure determination. X-ray study shows that the title compound has a weak intermolecular C—O... π interaction as well as many D—H...A and D—H... π hydrogen bonds. The initial guess on the compound was first obtained from the X-ray coordinates which were optimized by Density Functional Theory (DFT)/B3LYP method with 6-31G(d, p) and 6-31G+(d, p) as basis sets. DFT electronic structures were compared to the experimentally determined molecular structure in the solid state.

INTRODUCTION

In recent years, the synthesis and structural investigation 1,2,4-triazole derivatives have attracted considerable attention because of their pharmacological and biological properties such as antibacterial [1-3], antidepressant [4], antitubercular [5], analgesic [6], antiviral [7], etc. Cyclobutane itself is of no commercial or biological significance, but more complex derivatives are important in biology and biotechnology [8]. It is well known that 3-substituted cyclobutane carboxylic acid derivatives exhibit anti-inflammatory and anti-depressant activity [9], and also liquid crystal properties [10]. When these effects are taken into account, compounds containing 1,2,4-triazole and cyclobutane rings has become more remarkable.

In this study, a novel compound named as 2-((4,5-diphenyl-4H-1,2,4-triazol-3-yl)thio)-1-(3-methyl-3-phenylcyclobutyl)ethanone is firstly synthesized in our laboratories by us. Previously, we have reported the cyclobutane derivatives compound [11-12]. The difference of this study from the other studies, the molecular structure of the compound is supported by theoretical studies. Because it is given good results in the calculation of the molecular geometry, density functional theory (DFT) method was used in the theoretical calculations.

Our work makes up of the synthesis, X-ray molecular structure analysis and Density Functional Theory (DFT) studies of the title compound. The molecular structure of the title compound brought to light by X-ray diffraction. The initial guess of the compound was first obtained from the X-ray coordinates was optimized by DFT/B3LYP method with 6-31G(d, p) and 6-31G+(d, p) as basis sets. The calculated geometric parameters (bond lengths, bond angles and torsion angles) of theoretical structures were compared with their experimental data.

EXPERIMENTAL DETAILS

Synthesis of the Compound

A mixture of 4,5-diphenyl-4H-1,2,4-triazole-3-thiole (2.5332 g, 10 mmol) and 2-chloro-1-(3-methyl-3-phenylcyclobutyl)ethanone (2.2271 g, 10 mmol) in 10 mL of dry acetone was stirred for 2h (TLC) in the presence of 10 mmol anhydrous K₂CO₃. Solvent was evaporated under reduced pressure and the residue triturated with water. Thus obtained white precipitate separated by suction, washed with water several times, dried in air and crystallized from acetone. Yield: 83%, melting point: 462 K.

Crystal structures determination and refinement

A suitable sample of size 0.760 x 0.383 x 0.090 mm was selected for the crystallographic study. All diffraction measurements were performed at room temperature (296 K) using graphite monochromated Mo K α (λ = 0.71073 Å) radiation and an STOE IPDS 2 diffractometer. A total of 12978 reflections with [1.4° < θ < 25.7°] were collected in the rotation mode and cell parameters were determined by using X-Area software [13]. Absorption correction (μ =

0.17 mm⁻¹) was achieved by the integration method via X-RED software [13]. The structure was solved by direct methods using SHELXS-97 [14]. All non-hydrogen atoms were refined anisotropically by the full-matrix least squares procedure based on F² using SHELXL-97 [15]. All H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.93, 0.97 and 0.96 Å for CH, CH₂, and CH₃ atoms, respectively. The general purpose crystallographic tool PLATON [16] was used for the structure analysis and presentation of the results. The program ORTEP-3 [17] for Windows was used preparation of the figures.

Scheme Synthetic pathway for the synthesis of the target compound.

Theoretical calculations

All the calculations were performed by using Gaussian 03 package [18] and Gauss-View molecular visualization software [19] on the personal computer without restricting any symmetry for the title. For modeling, the initial guess of the compound was first obtained from the X-ray coordinates and this structure was optimized by Density Functional Theory (DFT)/B3LYP method with 6-31G(d, p) and 6-31G+(d, p) as basis sets. From the optimized geometry of the molecule, geometric parameters (bond lengths, bond angles, torsion angles) for the title compound have been calculated theoretically and compared with the experimental data. Besides, the frontier molecular orbital (FMOs), molecular electrostatic potential (MEP), and Mulliken charges were investigated.

RESULTS AND DISCUSSION

Molecular geometry

The atomic numbering scheme for the X-ray structure (C₂₅H₃₂N₃O₂S) and theoretical geometric structure of the title compound are shown in **Fig. 1**. X-ray diffraction analysis has revealed that the title compound crystallizes in orthorhombic system with space group C 2/c. The unit cell dimensions are a = 27.1633 (16) Å, b = 5.9555 (2) Å, c = 29.0936 (17) Å and V = 4614.6 (4) Å³. Details of the data collection conditions and the parameters of the refinement process are given in **Table 1**.

Table 1 Experimental details.

Crystal data	
Chemical formula	C ₂₇ H ₂₅ N ₃ OS
Formula weight (a.k.b.)	439.56
Temperature (K)	296
Crystal system	Monoklinik
Space group	C 2/c
Unit cell parameters	
a b c (Å)	27.1633(16), 5.9555(2), 29.0936(17)
$\alpha = \gamma \beta$ (°)	90.00, 101.339(5)
Crystal size (mm)	0.76 × 0.383 × 0.090
Volume, V (Å ³)	4614.6(4)
Z	1
μ (mm ⁻¹)	0.17
F ₀₀₀	1856
Calculated density (Mg/m ³)	1.265
Data collection	
Diffractionmeter	STOE IPDS-2
Wavelength (Å)	0.71073 Mo K α
θ range for data collection (°)	1.4 ≤ θ ≤ 25.7
Index ranges	
$h_{\min}^{\circ} h_{\max}^{\circ}$	-31, 32
$k_{\min}^{\circ} k_{\max}^{\circ}$	-6, 7
$l_{\min}^{\circ} l_{\max}^{\circ}$	-35, 35
Measurement method	ω taramasi
Reflections collected	12978
Independent reflections	4347
Observed reflections [$I > 2\sigma(I)$]	2537
Absorption correction	Integrasyon (X-RED32)
T _{min} [°] T _{max}	0.9473, 0.9892
R _{int}	0.041
Refinement	
Refinement method	SHELXL-97
Parameters	289
$R[F^2 > 2\sigma(F^2)]$	0.035
$wR(F^2)$	0.066
GooF = S	0.81
$\Delta\rho_{\min}^{\circ} \Delta\rho_{\max}^{\circ}$ (e/Å ³)	-0.16, 0.16

The title compound has “C₁” symmetry and contains a cyclobutane, a 1,2,4-triazole and three phenyl rings. It is composed of a 1,2,4-triazole ring, with an phenyl connected to the 2- and 4-position of the ring and a cyclobutane via S1, C14, C13 atoms in the 4-position. The dihedral angles between the cyclobutane plane A (C8-C11) and the 1,2,4-triazole plane B(N1/N2/C15/N3/C14) is 69.91 (9)°.

Cyclobutane ring has a butterfly conformation. The bond length between the carbon atoms average 1555 Å and bond angles formed by three carbon atoms are average 88° in this conformation [20]. For the title compound, these values was obtained as 1.554 Å and 88.42°, respectively. Also, when the bond lengths and angles of the cyclobutane ring in the compound are compared with the previously reported cyclobutane derivatives [21-22], it is seen that there are

no significant differences. Since the cyclobutane ring puckered to reduce the torsional stress, it is not planar. The amount of deviation from planar for the cyclobutane ring was found to be 0.1178 Å.

Figure 1: (a) A view of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. (b) The theoretical geometric structure of the title compound (B3LYP/6-31+G(d, p) level).

In the 1,2,4-triazole ring, the N—N bond length is 1.399 (2). This value is close to the corresponding value reported in literature value, 1.395 (2) Å [23]. The 1,2,4-triazole ring is planar with a maximum deviation of 0.0028 Å.

In the crystal structure, molecules are linked by many hydrogen bonds. The C13—H13B···N2, C11—H11···N2, C13—H13B···N1 and C25—H25···O1 interactions carried out formation of, and ring motifs, respectively. Perspective view of the C25—H25···O1 interactions in the unit cell is shown in Fig. 2. Crystal structure has three C—H··· π interactions. In these interactions, Cg1 and Cg2 rings are centre of phenyl and 1,2,4-triazole, respectively. Cg1 play a role as donor in the interaction of C7—H7B···Cg1 [symmetry code : -x, -2-y, -z] and C27—H27···Cg1 [symmetry code : x, -1+y, z], while Cg2 play a role as donor in the interaction of C20—H20···Cg2 [symmetry code : x, 2-y, -1/2+z]. The crystal structure is also stabilized by C—O··· π interactions between the C12, O1 atoms and 1,2,4-triazole ring [symmetry code: x, -1+y,

z]. The distance atom O1 between the centroids of these rings is 3.8029(19) Å. D—H, H···A, D···A lengths and D—H···A angles of these interactions in the crystal structure are listed in Table 2.

Figure 2: The packing in the unit cell of compound parallel to the (010) plane, showing the R₂²(22) rings. Dashed lines denote the intermolecular C—H···O hydrogen bondings. [Symmetry code: -x+1/2+1, -y-1/2, -z+1].

The molecular structure of the title compound was also calculated theoretically. The starting geometry was those obtained from the X-ray structure determination was optimized using Density Functional Theory (DFT/B3LYP)

method with the 6-31G(d, p) and 6-31G+(d, p) basis sets in ground state. The total energy, zero-point vibrational energy, entropy and dipole moment values obtained for optimized geometries are presented in **Table 3**.

Table 2 Hydrogen-bond geometry (Å, °) for the title compound.

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9A···O1	0.97	2.57	2.896 (2)	100
C13—H13B···N2 ^a	0.97	2.63	3.379 (2)	135
C11—H11···N2 ^a	0.98	2.69	3.563 (2)	149
C13—H13B···N1 ^a	0.97	2.68	3.512 (2)	144
C25—H25···O1 ^b	0.93	2.68	3.366 (2)	132
D—H···Cg	D—H	H···Cg	D···Cg	D—H···Cg
C20—H20···Cg1 ^c	0.93	2.87	3.711 (2)	150
C7—H7B···Cg2 ^d	0.96	2.91	3.745 (2)	146
C27—H27···Cg2 ^e	0.93	2.76	3.616 (2)	154
X—Y···Cg	X—Y	Y···Cg	X···Cg	X—Y···Cg
C12—O1···Cg3 ^d	1.198 (2)	3.8029(19)	3.8278(19)	82.14 (12)

Symmetry codes: (a) $-x+2, -y, -z+1$; (b) $-x+1/2+1, -y-1/2, -z+1$; (c) $-x, 2-y, -z$; (d) $x, -1+y, z$; (e) $x, 2-y, -1/2+z$. Cg1, Cg2 and Cg3 are the centroid of the C16-C21, C1-C6 and triazole rings, respectively.

The calculated D—H, H—A, D···A and D—H···A values for intramolecular C9—H9A···O1 interactions are 1.092 Å, 2.483 Å, 2.916 Å and 102.19 for B3LYP/6-31G(d, p) level and 1.093 Å, 2.516 Å, 2.932 Å and 101.23 for B3LYP/6-31G+(d, p) level, respectively.

Conventionally, two methods was used in comparison the molecular structures. The first method is to calculate the correlation value (R^2). The optimized geometrical parameters (bond lengths, bond angles and torsion angles) calculated by B3LYP/6-31G(d, p) and B3LYP/6-31G+(d, p) methods are listed in **Table 4**. We have created the correlation graph in **Fig. 3** based on the correlation calculations. Calculated R^2 values are 0.9929 and 0.9926 for bond lengths, 0.9835 and 0.9832 for bond angles, 0.9959 and 0.9948 for torsion angles at B3LYP/6-31G(d, p) and B3LYP/6-31G+(d, p) levels, respectively. According to correlations values, the B3LYP/6-31G+(d, p) method gave accurate results for the bond lengths, bond angles, torsion angles compared with the B3LYP/6-31G(d, p) method. The second method, comparing the structures obtained with the theoretical calculations is by superimposing the molecular skeleton with that obtained from X-ray diffraction, giving a RMSE of 0.204 Å and 0.222 Å for B3LYP/6-31G(d, p) and B3LYP/6-31G+(d, p) levels, respectively. (**Fig. 4**). According to these results, it may be concluded that the B3LYP/6-31G(d, p) calculation well reproduce the geometry of the title compound. While making these comparisons, it does not forget that the theoretical calculations carried out in gas phase.

Frontier molecular orbitals (FMOs)

The distributions of the HOMO and LUMO orbitals computed for the B3LYP/6-31G(d, p) and B3LYP/6-31G+(d, p) levels for the title compound are shown in **Fig. 5**. The calculations indicate that the title compound has 115 occupied molecular orbitals and the value of the HOMO and LUMO energies are -5.72 and -0.88 eV for B3LYP/6-31G(d, p) level, -6.01 and -1.23 eV for B3LYP/6-31G+(d, p) level, respectively. By using HOMO and LUMO energy values for a molecule, electronegativity, chemical hardness and chemical softness can be calculated as follows:

$$\chi = (I+A)/2 \text{ (electronegativity),}$$

$$\eta = (I-A)/2 \text{ (chemical hardness),}$$

$$S = 1/2\eta \text{ (chemical softness)}$$

where I and A are ionization potential and electron affinity;

$$I = -E_{\text{HOMO}}$$

$$A = -E_{\text{LUMO}}$$

respectively [24]. The HOMO and LUMO energies, the energy gap (ΔE), the ionization potential (I), the electron affinity (A), the absolute electronegativity (χ), the absolute hardness (η) and softness (S) for molecule have been calculated at the same levels and the results are given in **Table 5**.

Figure 3: Correlation graphics between the experimental and theoretical geometric parameters of the title compound.

Figure 4: Atom-by-atom superimposition of the structures calculated [B3LYP/6-31G(d, p)] (red) and [B3LYP/6-31G+(d, p)] (blue) over the X-ray structure (black) for the title compound. Hydrogen atoms omitted for clarity.

Figure 5: The distributions of the HOMO and LUMO orbitals computed at the B3LYP/6-31G(d, p) and B3LYP/6-31G+(d, p) levels for the title compound.

Table 3 The calculated thermodynamic parameters of the title compound.

Parametre	B3LYP/6-31G(d, p)	B3LYP/6-31G+(d, p)
Total energy (a.u.)	-1681.59711146	-1681.64018374
Zero-point vibrational energy (kcal/mol)	288.50014	287.87106
Entropy (cal/mol-K)	198.070	198.512
Heat capacity at const. volume (CV, cal/mol-K)	108.386	108.630
Rotational constants (GHz)		
A	0.29213	0.29135
B	0.04329	0.04315
C	0.04054	0.04050
Dipole Moment (Debye)		
	-0.9910	-1.1055
	1.8260	-1.7819
	0.8777	0.9189
	2.2554	2.2895

Molecular electrostatic potential (M.E.P.)

The molecular electrostatic potential (MEP) of compound was determined using B3LYP/6-31G(d, p) and B3LYP/6-31G+(d, p) levels (**Fig. 6**). The color code of these maps are in the range between -0.063 a.u. (red) to 0.063 a.u. (blue) for B3LYP/6-31G(d, p) and -0.061 a.u. (red) to 0.061 a.u. (blue) for B3LYP/6-31G+(d, p). The negative (red color) regions are mainly localized on the atoms O1, N1 and N2. These settlement predicts that atoms in these regions act as acceptor in hydrogen bondings. **Fig. 6** confirms the intramolecular and intermolecular hydrogen bondings in **Table 2**.

Figure 6: Molecular electrostatic potential (MEP) map in gas phase of compound.

Mulliken population analysis

The Mulliken charge distributions of compound was calculated using B3LYP/6-31G(d, p) and B3LYP/6-31G+(d, p) levels. The calculated charge for all atoms has been given in **Figure 7**. It is well-known that the Mulliken charges confirm the hydrogen bonding in the molecular structure of compound. For the title compound, the Mulliken charge corresponding to the atoms in hydrogen bondings is shown in **Table 6**.

Table 4 Some selected geometric parameters of the title compound.

Geometric Parameters	Experimental [X-ray]	Calculated [B3LYP]	
		6-31G(d, p)	6-31G+(d, p)
Bond lengths (Å)			
C1—C2	1.388 (3)	1.398	1.397
C2—C3	1.368 (3)	1.391	1.398
C6—C8	1.508 (2)	1.518	1.518
C7—C8	1.533 (2)	1.539	1.541
C8—C9	1.548 (2)	1.562	1.563
C11—C12	1.489 (2)	1.515	1.514
C12—O1	1.198 (2)	1.217	1.219
C12—C13	1.497 (2)	1.518	1.519
C13—S1	1.793 (2)	1.833	1.833
S1—C14	1.735 (2)	1.765	1.764
C14—N1	1.305 (2)	1.315	1.315
N1—N2	1.399 (2)	1.378	1.378
N2—C15	1.307 (2)	1.316	1.316
C15—C16	1.466 (2)	1.470	1.471
C16—C17	1.392 (2)	1.406	1.407
N3—C22	1.442 (2)	1.433	1.435
C22—C23	1.377 (2)	1.398	1.398
Bond Angles (°)			
C9—C8—C10	87.75 (13)	87.16	88.17
C8—C9—C11	89.66 (14)	89.73	89.64
C11—C12—C13	116.76 (15)	115.57	115.25
C13—S1—C14	99.65 (8)	96.46	96.75
C14—N3—C15	104.37 (12)	104.03	104.12
C14—N1—N2	106.44 (13)	107.25	107.31
C15—N2—N1	107.99 (13)	108.52	108.52
Torsion Angles (°)			
N2—C15—C16—C17	29.7 (2)	27.14	29.59
C1—C6—C8—C10	48.7 (2)	42.46	42.51
C8—C9—C11—C10	17.38 (14)	16.16	16.45
C10—C11—C12—O1	92.0 (3)	89.74	91.98
C27—C22—N3—C14	66.0 (2)	71.73	73.45
N3—C22—C23—C24	179.23 (15)	179.67	179.6

Table 5 The calculated frontier orbital energies, ionization potential (I), electron affinity (A), absolute electronegativity (χ), absolute hardness (η) and softness (S) of compound using B3LYP/6-31G(d, p) and B3LYP/6-31G+(d, p) levels.

Parameters	B3LYP/6-31G(d, p)	B3LYP/6-31G+(d, p)
	-5.72	-6.01
	-0.88	-1.23
	5.72	6.01
	0.88	1.23
	3.30	3.62
	2.42	2.39
	0.21	0.21

Table 6 The calculated Mulliken charges of the hydrogen bondings in the crystal structure.

D—H...A	B3LYP/6-31G(d, p)			B3LYP/6-31G+(d, p)		
	D	H	A	D	H	A
C9—H9A...O1	-0.275	0.159	-0.434	-0.359	0.185	-0.469
C13—H13B...N2	-0.206	0.179	-0.361	-0.299	0.221	-0.316
C11—H11...N2	-0.162	0.126	-0.361	-0.258	0.141	-0.316
C13—H13B...N1	-0.206	0.179	-0.343	-0.299	0.221	-0.317
C25—H25...O1	-0.272	0.107	-0.434	-0.258	0.102	-0.469
C—H...Cg	D	H	Cg	D	H	Cg
C20—H20...Cg1	-0.097	0.121	-0.334	-0.279	0.128	-0.394
C7—H7B...Cg2	-0.304	0.111	-0.347	-0.283	0.156	-0.199
C27—H27...Cg2	-0.069	0.149	-0.347	-0.189	0.135	-0.199

Figure 7: The charge distribution calculated by the Mulliken method for the title compound.

CONCLUSION

The title compound, 2-((4,5-diphenyl-4H-1,2,4-triazol-3-yl)thio)-1-(3-methyl-3-phenylcyclobutyl) ethanone, was investigated both experimentally and theoretically. The important conclusions to be obtained from this study are as following:

1. The compound was synthesized and its molecular structure by single-crystal X-ray diffraction method has been brought to light in our laboratory. The crystal structure and geometric parameters of the compound was obtained with high accuracy.

2. The initial assumption of the compound was first obtained from the X-ray coordinates was optimized by Density Functional Theory (DFT)/B3LYP method with 6-31G(d, p) and 6-31G+(d, p) as basis sets. It was compared the calculated molecular geometries with their X-ray data and an excellent harmony between the two data was ascertained.

3. The frontier molecular orbitals (HOMO and LUMO) and related to parameters was generated by theoretical results.

4. The Molecular electrostatic potential (MEP) map shows that the

negative potential sites are on electronegative atoms and the positive potential sites are around the hydrogen atoms. The calculated maps for the title compound verify the hydrogen bondings in the crystal structure.

5. The calculated Mulliken charges confirm the hydrogen bondings in the crystal structure.

It was noted here that the experimental results belong to solid phase and theoretical calculations pertain to gaseous phase.

REFERENCES

- 1- D. J. Prasad, M. Ashok, P. Karegoudar, B. Poojary, B. S. Holla and N. S. Kumari, *Eur. J. Med. Chem.*, 44, 551-557 (2009).
- 2- A. Foroumadi, S. Mansouri, Z. Kiani and A. Rahmani, *Eur. J. Med. Chem.*, 38, 851-854 (2003).
- 3- V. J. Ram, L. Mishra, N. H. Pandey, D. S. Kushwaha, L. A. C. Pieters and A. J. Vlietinck, *J. Heterocyclic Chem.*, 27, 351-355 (1990).
- 4- J. E. Przeglądski and A. Lewandowska, *J. Neural Transm.*, 46, 303-312 (1979).
- 5- I. Küçükgül, S. G. Küçükgül, S. Rollas and M. Kiraz, *Bioorg Med Chem Lett.*, 11, 1703-1707 (2001).
- 6- G. Turan-Zitouni, Z. Kaplancikli, K. Erol and F. Kiliç, *Il Farmaco*, 54, 218-223 (1990).
- 7- M. Kritsanida, A. Mouroutsou, P. Marakos, N. Pouli, S. Papakonstantinou-Garoufalias, C. Pannecouque, M. Witvrouw and E. De Clercq, *Il Farmaco*, 57, 253-257 (2002).
- 8- <http://en.wikipedia.org/wiki/Cyclobutane>, 01.06.2015.
- 9- E. V. Dehmlow and S. Schmidt, *Liebigs Annalen der Chemie*, 5, 411-414, (1990).
- 10- L. Coghi, A. M. M. Lanfredi ve A. Tiripicchio, *Journal of the Chemical Society, Perkin Transactions 2*, 1808-1810, (1976).
- 11- F. Şen, M. Dinçer, A. Cukurovali ve I. Yilmaz, *Acta Cryst.*, E67, o958-o959, (2011).
- 12- F. Şen, M. Dinçer, A. Cukurovali and I. Yilmaz, *Acta Cryst.*, E68, o1052, (2012).
- 13- S. & Cie, X-AREA (Version 1.18) and X-RED32 (Version 1.04), Darmstadt, (2002).
- 14- G. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, (1997).

- 15- G. Sheldrick, SHELXL-97, Program for Crystal Structures Refinement, University of Göttingen, (1997).
- 16- A. L. Spek, *Acta Cryst.*, D65, 148-155, (2009).
- 17- L. J. Farrugia, *J. Appl. Crystallogr.*, 45, 849-854, (2012).
- 18- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. J. A. Montgomery, 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, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, A. Austin, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. 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 and J. A. Pople, Gaussian 03, Revision E.01, Wallingford CT: Gaussian, Inc., (2004).
- 19- R. Dennington II, T. Keith, and J. Millam, Gauss View Version 4.1.2, Shawnee Mission, Kansas: Semichem Inc., (2007).
- 20- T. W. G. Solomons and C. B. Fryhle, Organic Chemistry, 7 dü., New York: John Wiley & Sons, (2002).
- 21- E. İnkaya, M. Dinçer, Ö. Ekici and A. Çukurovalı, *Spectrochim. Acta A*, 101, 218-227 (2013).
- 22- E. İnkaya, M. Dinçer, Ö. Ekici and A. Çukurovalı, *J. Mol. Struct.*, 1026, 117-126, (2012).
- 23- M. Dinçer, N. Özdemir, A. Çetin, A. Cansız and O. Büyükgüngör, *Acta Cryst.*, C61, o665–o667, (2005).
- 24- R. G. Pearson, *Proc Natl Acad Sci USA*, 83, 8440-8441, (1986).