ISSN 1063-7745, Crystallography Reports, 2017, Vol. 62, No. 7, pp. 1122–1127. © Pleiades Publishing, Inc., 2017.

STRUCTURE OF ORGANIC COMPOUNDS

Experimental (X-ray, FT-IR, and UV-Vis Spectroscopy) and Theoretical Methods (DFT Study) of N'-(Dipyridin-2-ylmethylene)-4-methylbenzenesulfonohydrazide[1]

Erbil Murat Aydın[a], Murat Çınarlı[b], Hümeyra Batı[c], Nezihe Çalışkan[a,*], and Çiğdem Yüksektepe Ataol[d]

[a] *Department of Physics, Faculty of Sciences, Gazi University, Ankara, 06500 Turkey*

[b] *Central Research and Application Laboratory, Ahi Evran University, Kırşehir, 40100 Turkey*

[c] *Department of Chemistry, Faculty of Science, Ondokuz Mayis University, Samsun, 55139 Turkey*

[d] *Department of Physics, Faculty of Sciences, Cankiri Karatekin University, Cankiri, 18100 Turkey*

**e-mail: ncaliskan@gazi.edu.tr*

Received February 22, 2016

Abstract—A new hydrazone derivative was synthesized and characterized by IR, UV-Vis spectroscopy, elemental analysis and single-crystal X-ray diffraction. The compound was established to reveal antibacterial activity. The compound ($C_{18}H_{16}N_4O_2S$) crystallizes in monoclinic crystal system with $C2/c$ space group. The molecular structure is stabilized by a C–H···O intermolecular hydrogen bond. Quantum chemical calculations based on DFT/B3LYP/6-31G(d, p) were carried out and the results were compared with the experimental data. The calculated vibrational frequencies were used to determine the types of molecular motions associated with each of the observed experimental bands. UV-Vis absorption spectra of the compound calculated by TD-DFT have been ascribed to their corresponding molecular structure and electron transitions.

DOI: 10.1134/S1063774517070045

INTRODUCTION

It is well-known that sulfonamides and sulfonylhydrazones exhibit a broad spectrum of biological activities such as antimicrobial [1, 2], antitumor [3], antidepressant-like activity [4], therefore, scientist have directed considerable attention on their synthesis, bioactivity and computational studies [5–7]. Transition metal complexes of hydrazides and sulfonamides as well as their hydrazone derivatives also find application in chemotherapy [8].

A number of papers devoted to the calculation of vibrational assignments by quantum-chemistry methods have recently appeared in the literature [9–13]. These papers indicate that geometry optimization is a crucial factor in an accurate determination of calculated vibrational frequencies. Moreover, it is known that the density functional theory (DFT) adequately takes into account electron correlation contributions, which are especially important in systems containing extensive electron conjugation and/or electron lone pairs. It was proposed that the single-point calculation of magnetic shielding by DFT methods was combined with a fast and reliable geometry-optimization procedure at the molecular mechanics level [14]. In most cases, in order to take into account correlation effects, post-Hartree-Fock calculations of organic molecules have been performed using (i) Møller-Plesset perturbation methods, which are very time consuming and, hence, applicable only to small molecular systems, and (ii) DFT methods, which usually provide significant results at a relatively low computational cost. In this regard, DFT methods have been preferred in the study of large organic molecules, metal complexes and organometallic compounds in all those cases, in which the electron correlation contributions were not negligible.

In this study, we present results of a detailed investigation of synthesis and structural characterization of the title compound N'-(dipyridin-2-ylmethylene)-4-methylbenzenesolfonohydrazide ($C_{18}H_{16}N_4O_2S$) (**I**) using single crystal X-ray diffraction, IR and UV-Vis spectroscopy and quantum chemical methods. The vibrational assignments, and frontier molecular orbitals (FMO) analysis of the title compound in the ground state have been calculated using the DFT(B3LYP) methods and TD-DFT with 6-31G(d, p) basis sets, respectively. The initial geometry of the compound for all calculations was taken from the X-ray refinement data. A comparison of the experimental and theoretical spectra can be very useful in making correct assignments and understanding the molecular structure relationship. Thus, these calcula-

[1] The article is published in the original.

Table 1. Results of elemental analysis for the compound **I**

Compound	M_A, g/mol	Colour	Calculated/found, %			
			C	H	N	S
$C_{18}H_{16}N_3O_2S$	352	Yellow	61.36/60.29	4.54/4.49	15.90/15.53	9.09/8.84

tions are valuable for providing insight into molecular analysis. The results from both experimental and theoretical calculations are compared and the computed geometrical and spectroscopic parameters are in good agreement with the experimental results.

EXPERIMENTAL

Materials and Methods

All material used in this study were purchased from Sigma-Aldrich and used as received. The electronic absorption spectra of title compound **I** were recorded at room temperature in methanol solution on a Unicam UV2 UV-Vis spectrometer working at 200–800 nm. IR spectra were recorded on a JASKO FT/IR-430 Fourier transform-infrared (FT-IR) spectrometer using KBr pellets. Elemental analysis was recorded on Thermo Flash 2000 Elemental Analyzer (Table 1).

*Synthesis of Compound **I***

Compound **I** was synthesized as shown in Fig. 1 by the following procedure. Preparation of the compound (**I**): *p*-toluenesulfonylhydrazide (0.093 g, 0.5 mmol) was dissolved in methanol. To this solution was added dropwise di-2-pyridylketone (0.094 g, 0.5 mmol) in methanol. The mixture was refluxed for 2–3 h and cooled down. Yellow crystalline compound separated out.

X-ray Diffraction

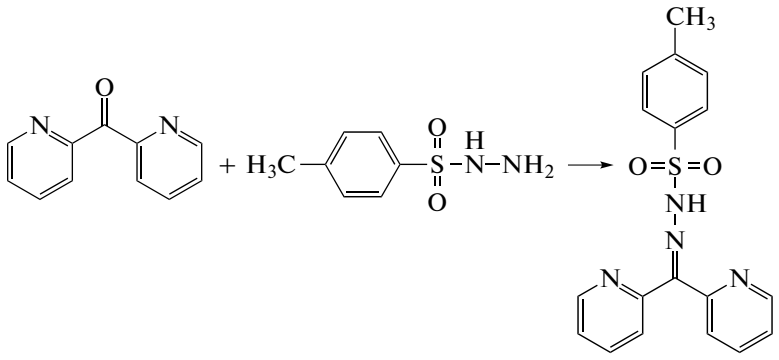
The data collection was performed at 296 K on a Stoe-IPDS-2 diffractometer equipped with a graphite monochromated MoK_α radiation (λ = 0.71073 Å). The structure was solved by direct methods using SHELXS-97 [15] and refined by a full-matrix least-squares procedure using the SHELXL-2013 program [16]. All non hydrogen atoms were refined anisotropically. The hydrogen atoms were place in calculated positions and refined in isotropic approximation with C–H = 0.93 Å (for pyridine and phenyl groups) and N–H = 0.86 Å, U_{iso}(H) = 1.2U_{eq}(C, N). Crystallographic data for the title compound has been deposited with Cambridge Crystallographic Data Centre (CCDC no. 967687). This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

DFT Calculations

All calculations were performed using Density Functional Theory DFT B3LYP [17, 18] level with the 6-31G (*d*, *p*) basis set. We have used the Gaussview molecular visualization program [19] and the Gaussian 03 program [20] to perform DFT calculations.

*Detection of Antimicrobial Activity of Compound **I***

The bacterial subcultures chosen were *Enterobacter aerogenes* sp., *Listeria monocytogenes* 4b ATCC19115, *Staphylococcus aureus* ATCC25923, *Escherichia coli*



N'-(Dipyridin-2-ylmethylene)-4-methylbenzenesulfonohydrazide

Fig. 1. Synthetic route for the synthesis of target compound.

ATCC1280, S *Salmonella typhi* H NCTC901.8394, *Staphylococcus epidermis* sp., *Micrococcus luteus* ATCC9341, *Shigella dysenteria type* 2 NCTC2966, *Bacillus cereus* RSKK-863. An antifungal susceptibility test was used by *Candida albicans* Y-1200-NIH, Tokyo.

The synthesized compound was examined for its antimicrobial activity by the well-diffusion method [21]. Compound **I** was kept dry at room temperature and dissolved (25, 100, and 200 μg/mL) in DMSO. DMSO was used as both solvent and control. It was found to have no antimicrobial activity against any of the tested organisms 1% (v/v) of a 24 h broth culture containing 10^6 CFU/mL was placed in the sterile Petri dishes. Mueller-Hinton Agar (MHA) (15 mL) kept at 45°C was then poured in to the Petri-dishes and allowed to solidify. Then wells of 6 mm diameter were punched carefully using a sterile cork borer and were entirely filled with the test solutions. The plates were incubated for 24 h at 37°C. On completion of the incubation period, the mean value obtained for the two holes was used to calculate the zone of growth inhibition of each sample. Bacterial subcultures and yeast were tested for resistance to five antibiotics produced by Oxoid Lt., Basingstoke, UK. These were: Ampicillin (prevents the growth of Gram-negative bacteria), Nystatin (binds to sterols in the fungal cellular membrane and alters the permeability allowing leakage of the cellular contents), Sulphamethoxazol (a bacteriostatic antibacterial agent that interferes with folic acid synthesis in susceptible bacteria).

Table 2. Crystallographic data for the compound **I**

Empirical formula	$C_{18}H_{16}N_4O_2S$
Formula weight	352.41
System, sp. gr., Z	monoclinic, $C2/c$, 8
a, b, c, Å	26.3776(9), 9.0450(3), 20.0630(7)
β, deg	134.874(2)
V, Å^3	3392.2(2)
Radiation, λ, Å	MoK_α, 0.71073
μ, mm^{-1}	0.210
T, K	296
T_{min}, T_{max}	0.7860, 0.9537
Crystal size, mm^3	0.320 × 0.443 × 0.530
θ range, deg	2.04–25.00
h, k, l ranges	$-31 \le h \le 31$, $-10 \le k \le 10$, $-23 \le l \le 23$
Measured reflections	16081
Independent reflections	2994
Observed reflections ($I > 2\sigma(I)$)	2624
S	1.19
R_1 ($I > 2\sigma(I)$)	0.068
wR_2 ($I > 2\sigma(I)$)	0.12

RESULTS AND DISCUSSION

Molecule Structure

The title compound contains pyridine rings, hydrazone, and phenyl moieties. Details of crystal parameters, data collection, structure solution and refinement are given in Table 2. Molecular structure of **I** is shown in Fig. 2. There are two pyridine rings and one phenyl ring in the molecule. Phenyl ring C1···C6 is denoted as *A*, pyridine ring C9···C13, N3 as *B*, and pyridine ring C14···C18, N4 as *C*. The dihedral angles between these rings are 57.87(8)° for *A*/*B*, 86.78(9)° for *A*/*C*, 56.32 (11)° for *B*/*C*. Selected bond distances, bond angles and dihedral angles are listed in Table 3. Vast majority of them are close to the standard values within the corresponding standard deviations. In the hydrazone group, the C8=N2 double bond distance of 1.297(3) Å is in good agreement with the C=N bond distance found in the related hydrazone structure [13]. The torsion angle (C8–N2–N1–S1) equal to 169.9° points out near planarity of sulfonohydrazide moiety.

DFT Calculations

We have calculated theoretical structural parameters and vibrational spectra of the title compound using the B3LYP method with 6-31G(*d*, *p*) basis set. We have compared experimental and calculated results. The experimental and calculated bond lengths and angles slightly differ from each other are shown in Table 3. This difference stems from that theoretical

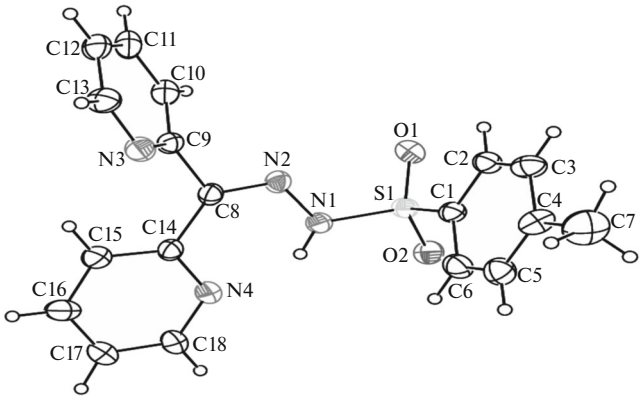


Fig. 2. Molecule of the title compound **I** with atom labeling.

Table 3. Optimized and experimental geometric parameters for the compound **I**

Atoms	Experimental	Calculated (B3LYP)
Bond lengths, Å		
S1–O1	1.425(2)	1.459
S1–O2	1.426(2)	1.463
S1–C1	1.760(2)	1.790
S1–N1	1.631(2)	1.704
N1–N2	1.371(2)	1.336
N2–C8	1.297(3)	1.302
N3–C9	1.337(3)	1.344
N3–C13	1.337(3)	1.339
N4–C14	1.339(3)	1.353
N4–C18	1.333(3)	1.336
C1–C6	1.385(3)	1.395
C5–C6	1.376(4)	1.394
C8–C9	1.496(3)	1.496
C8–C14	1.482(3)	1.489
C16–C17	1.362(4)	1.395
C17–C18	1.365(3)	1.392
Bond angles, deg		
S1–C1–C6	119.0(2)	119.26
O1–S1–C1	107.8(1)	107.92
O1–S1–O2	120.0(1)	122.92
O2–S1–C1	108.3(1)	108.58
N1–S1–O1	109.15(9)	107.7
N1–S1–O2	104.01(9)	102.8
N1–S1–C1	106.9(1)	105.67
N1–N2–C8	119.3(2)	122.38
N2–N1–S1	116.3(1)	117.38
C9–C8–C14	119.1(2)	121.82
C9–N3–C13	116.8(2)	118.26
Torsion angles, deg		
N1–S1–C1–C6	64.9(2)	96.9
N1–S1–C1–C2	−116.8(2)	−82.5
N1–N2–C8–C9	−178.2(2)	−179.1
N1–N2–C8–C14	0.7(3)	0.2
N2–N1–S1–C1	72.1(2)	67.6
N2–N1–S1–O1	−44.3(2)	−47.6
C2–C1–S1–O2	131.6(2)	167.8
C6–C1–S1–O1	−177.9(2)	−148.1
C8–N2–N1–S1	−169.9(2)	−173.03

Table 4. Comparison of the experimental and calculated vibrational frequencies of the compound **I**

Assignment[a]	Experimental, cm^{-1}	B3LYP/6-31G(*d*, *p*), cm^{-1}
ν(NH)	3174	3284
$\nu_{as}(CH_3)$	3055	3102
$\nu_s(CH_3)$	–	3041
ν_s(CN) sch. base	1582	1592
δ (NH)	1429	1401
$\nu_{as}(S–O_2)$	1333	1361
ν(CN) pyr. ring	1303	1321
ν_s(NN) sch. base	1166	1162
$\nu_s(S–O_2)$ + δ(CH) phe.	1090	1089
δ(NH) out of plane	744	706

[a] Pyr: pyridine, sch. base: Schiff base, phe: phenyl, ν: stretching, ν_s: symmetric stretching, ν_{as}: asymmetric stretching, δ: bending.

calculations were carried out for an isolated molecule in gaseous phase, whereas experimental data were obtained for a molecule in the solid phase. As can be seen from Table 3, theoretically calculated and experimental results are in good agreement with each other. For instance, the experimental N1–N2 bond length is 1.371(2) Å and the calculated one, 1.336 Å; these values are also close to literature ones [22, 23].

The experimental FT-IR spectrum is shown in the Fig. 3. In Table 4, theoretical calculated and experimental vibrational frequencies of the title compound are compared. The calculated frequencies were not scaled. According to the analysis of experimental data, the absorption band centered at 3174 cm^{-1} is assigned to the ν(N–H) stretching vibration of hydrazone group. Also, this band was calculated at 3284 cm^{-1}, which is in good agreement with literature values [24, 25]. The experimental O–S–O asymmetric and symmetric stretching vibrations were observed at 1332 and 1090 cm^{-1}, respectively, and calculated at 1361 and 1089 cm^{-1}, respectively.

Table 5. Molecular orbital energies of the compound **I**

Energies	B3LYP/6-31G(*d*, *p*)
HOMO, a.u.	−0.229
LUMO, a.u.	−0.061
Δ, a.u. (eV)	0.168 (4.57)
HOMO−1, a.u.	−0.254
LUMO+1, a.u.	−0.031

1 a.u. = 27.2116 eV

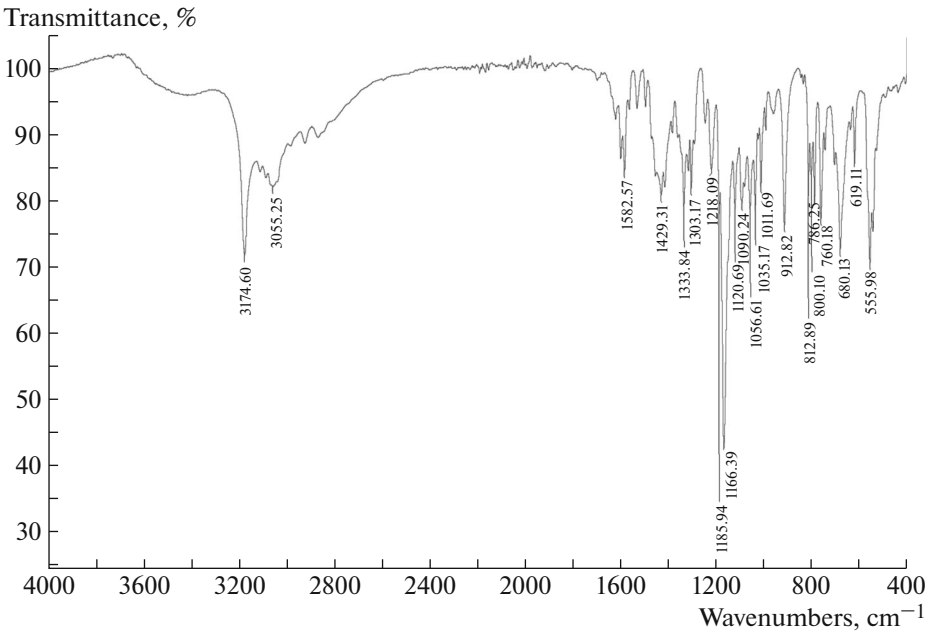


Fig. 3. IR spectrum of the compound **I**.

We have calculated molecular orbital (MO) energies by using TD-DFT/B3LYP/6-31G(*d*, *p*). The title compound has 92 occupied MOs. Some of them are the highest-occupied molecular orbital (HOMO), the lowest-unoccupied molecular orbital (LUMO), the second-highest occupied molecular orbital (HOMO–1) and the second lowest-unoccupied molecular orbital (LUMO+1). Figure 4 shows the HOMO–1, HOMO, LUMO, LUMO+1 and the corresponding energy levels for the title compound **I**. In addition, these MOs and band gap energies are given in Table 5. As can be seen from Fig. 4, there are electron-densities delocalized onto the pyridine and hydrazone groups in both the HOMO and LUMO. However, the extent of electron-density delocalization in the HOMO–1 is onto both the phenyl ring and the sulfono group. Futhermore, electron-density in the LUMO+1 is delocalized onto the pyridine ring.

Figure 5 shows the UV-Vis experimental absorption spectra of the title compound. The absorption peaks of the title compound observed at 222, 268, and 301 nm. The peak at 222 nm corresponds to $\pi \rightarrow \pi^*$ transitions. Furthermore, the peaks at 268 and 301 nm correspond to $n \rightarrow \pi^*$ transitions. When we compared the experimental and calculated electronic transitions, the absorption band at 4.12 eV (301 nm) is attributed to the HOMO → LUMO transition which has 0.168 a.u. (4.57 eV) energy gap and other absorption band at 5.58 eV (222 nm) is attributed to the HOMO → LUMO+1 transitions which has 0.198 a.u. (5.39 eV) energy gap.

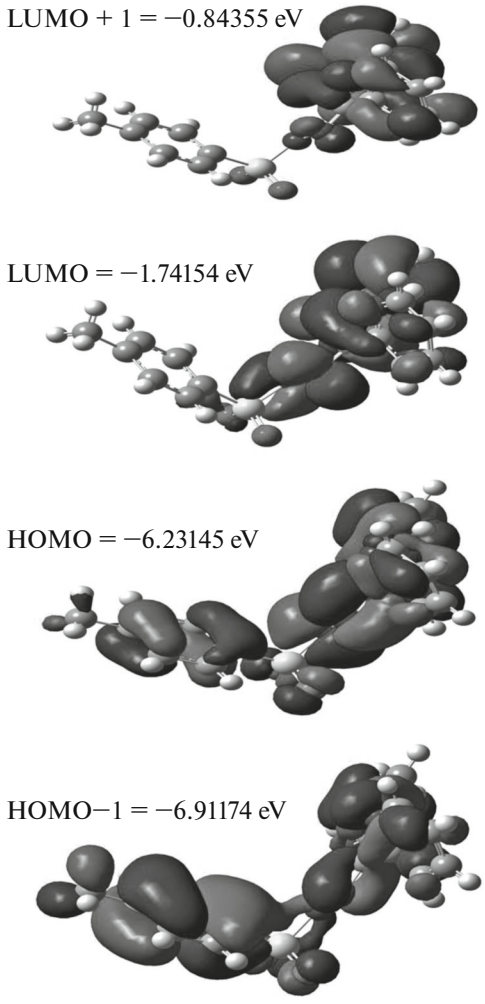


Fig. 4. 3D plots of the molecular orbitals for the compound **I**.

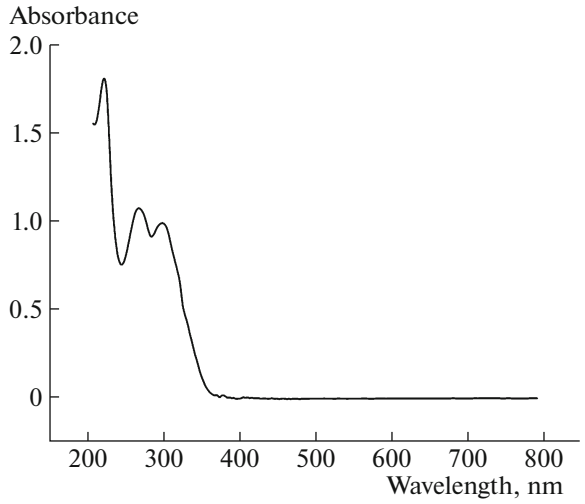


Fig. 5. The experimental UV-Vis spectrum of the compound **I**.

Antibacterial Assays

In general, compound **I** has antimicrobial activities on *E. Aerogenes, C. Albicans, P. Aeruginosa, and M. Luteus*. Antibacterial effects of compound **I** are given Table 6. Compound **I** is more active than standarts on the certain bacteria.

Table 6. Antibacterial effects of the compound **I**

	Compound **I**			AMP10	SXT25	NYS100
μg/mL	25	100	200			
E. aerogenes	17	19	20			
S. epidermidis	12	18	20			
P. aeruginosa	–	19	20			
S. aureus	–	12	13	30	24	
B. cereus	–	14	20			
C. albicans	26	22	24	–	–	20
M. luteus	15	18	19			
S. typhi h	14	16	19	11	17	
E. coli	–	12	15	10	18	
Sh. Dys 2	12	16	–			
L. monocytogenes	15	13	15			

REFERENCES

1. C. M. Sharaby, Spectrochim. Acta A **66**, 1271 (2007).
2. C. M. Sharaby, G. G. Mohamed, and M. M. Omar, Spectrochim. Acta A **66**, 935 (2007).
3. N. S. El-Sayed, E. R. El-Bendary, S. M. El-Ashry, et al., Eur. J. Med. Chem. **46**, 3714 (2011).
4. K. N. de Oliveira, P. Costa, J. R. Santin, et al., Bioorg. Med. Chem. **19**, 4295 (2011).
5. A. Chandran, Y. S. Mary, H. T. Varghese, et al., Spectrochim. Acta A **79**, 1584 (2011).
6. M. Karabacak, E. Postalcilar, and M. Cinar, Spectrochim. Acta A **85**, 261 (2012).
7. H. Alyar, A. Ünal, N. Özbek, et al., Spectrochim. Acta A **91**, 39 (2012).
8. G. V. Tsintsadze, R. S. Kurtanidze, M. A. Mdivani, et al., *Problems of Modern Bioinorganic Chemistry* (Nauka, Moscow, 1986), p. 211.
9. M. Dinçer, D. Avcı, M. Şekerci, et al., J. Mol. Model **14**, 823 (2008).
10. N. Özdemir, M. Dinçer, A. Çukurovalı, et al., J. Mol. Model **15**, 1435 (2009).
11. N. Misra, O. Prasad, L. Sinha, et al., J. Mol. Struct. (Theochem) **822**, 45 (2007).
12. F. Jian, P. Zhao, H. Guo, et al., Spectrochim. Acta A. **69**, 647 (2008).
13. J. Choo, S. Yoo, S. Moon, et al., Vibr. Spectrosc. **17**, 173 (1998).
14. D. A. Forsyth and A.B. Sebag, J. Am. Chem. Soc. **119**, 9483 (1997).
15. G. M. Sheldrick, *SHELXS-97 and SHELXL-97* (University of Göttingen, Göttingen, 1997).
16. G. M. Sheldrick, *SHELXS-2013* (University of Göttingen, Göttingen, 2013).
17. A. D. Becke, J. Chem. Phys. **8**, 5648 (1993).
18. P. J. Stephens, F. J. Devlin, and M. J. Frisch, J. Phys. Chem. **98**, 11623 (1994).
19. A. Frish, A. B. Nielseni, and A. J. Holder, *Gaussview User Manual* (Gaussian, Pittsburg, 2001).
20. M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., *GAUSSIAN 03, Revision B.02* (Wallingford, CT, 2004).
21. A. R. Yaul, V. V. Dhande, and A. S. Aswar, Rev. Roum. Chim **55** (9), 537 (2010).
22. Ç. Yüksektepe, H. Saraçoğlu, N. Çalışkan, et al., Mol. Cryst. Liq. Cryst. **533**, 126 (2010).
23. F. Güntepe, H. Saraçoğlu, N. Çalışkan, et al., J. Struc. Chem. **52**, 596 (2011).