Characterization and Structural Investigations of Schiff Based Pentafluorinated Derivative Compound

Sevgi Kansız*[1] and Necmi Dege[2]

[1]*Department of Fundamental Sciences, Samsun University, Turkey*
[2]*Department of Physics, Ondokuz Mayıs University, Turkey*

(sevgi.kansiz@samsun.edu.tr) Email of the corresponding author

Abstract – Schiff-based compounds continue to be involved in the work of many researchers because they are used as catalysts, pigments and dyes, and as intermediates in organic synthesis, as well as exhibiting a wide range of biological activities including antibacterial, antiviral and antipyretic properties. The pentafluorinated derivative Schiff-based compound crystallized in the monoclinic crystal system $P2_1/c$ space group with a=12.1048 (10) Å, b=7.3995 (4) Å, c=12.8768 (10) Å, $\alpha = \gamma = 90°$, $\beta = 95.852$ (6)° and Z=2 unit cell parameters. The pentafluorobenzene ring and the phenol ring are twisted at a dihedral angle of 40.14 (5)°, the molecule is not planar. The compound exhibiting the S6 ring motif with O−H⋯N intramolecular hydrogen bond exists in the enol tautomeric form. There is intermolecular C−H⋯F bond interaction in the compound. In addition, weak $\pi\cdots\pi$ interactions in the compound form a three-dimensional structure in the *ac* plane and along the *b* axis. Furthermore, Hirshfeld surface analysis was performed for the accuracy of supramolecular interactions in the compound. The results show that the most important contributions in the crystal packing are F⋯H (43.2%), C⋯C (12.5%), F⋯F (9.2%), and H⋯H (9%) proved to be due to their interactions. In the crystal, the dispersion energy framework contributes more to the total energy framework. The density functional method and Becke type three-parameter Lee-Yang-Par model (B3LYP) and the 6-311G(d,p) basis set were used in the theoretical calculations. HOMO-LUMO energies, chemical hardness and softness parameters, and molecular electrostatic potential (MEP) map were created, and the results were evaluated.

Keywords – Crystal structure, Schiff Based, Pentafluorophenol, Hirshfeld Surface Analysis, DFT.

I. INTRODUCTION

Schiff bases are compounds that are obtained from the nucleophilic addition reaction of aldehydes or ketones with amines and contain carbon-nitrogen double bonds (-CH=N-). The bond formed as a result of its reaction with aldehyde is called azomethine or aldimine, while the bond formed as a result of its reaction with ketone is called imine or ketamine. Schiff bases (imines) have succeeded in being among the compounds of interest because they are stable and easily synthesized. This interest in imines can be explained by their use in many biological systems, chemical catalysis, medicine and pharmacy, chemical analysis, and new technologies [1-3]. Schiff-based compounds continue to be involved in the work of many researchers because they are used as catalysts, pigments and dyes, and as intermediates in organic synthesis, as well as exhibiting a wide range of biological activities including antibacterial, antiviral and antipyretic properties [4-8].

In this study, a nitrogen containing pentafluorinated derivative Schiff-based compound, [(pentafluoro-benzylidene)amino] phenol, was determined by X-ray diffraction technique. HOMO, LUMO, and ΔE (E_{LUMO} – E_{HOMO}) energy values of the geometry optimized structure were calculated. A molecular electrostatic potential map (MEP) was created. In addition, Hirshfeld surface analysis and interaction energies of the compound were investigated to examine intermolecular interactions.

II. MATERIALS AND METHOD

X-ray reflection data of the compound was collected with the STOE IPDS 2 diffractometer [9]. The molecular structure of the compound was elucidated using the SHELXT crystallographic package program [10]. In addition, the molecular structure was improved by refining with SHELXL [11]. Theoretical calculations were performed using the Gaussian 09W program with the DFT method [12,13]. The compound was optimized at the B3LYP/6-311G(d,p) level, and quantum mechanical data were obtained in the gas phase. The Hirshfeld surface analysis was performed using CrystalExplorer17.5 [14,15].

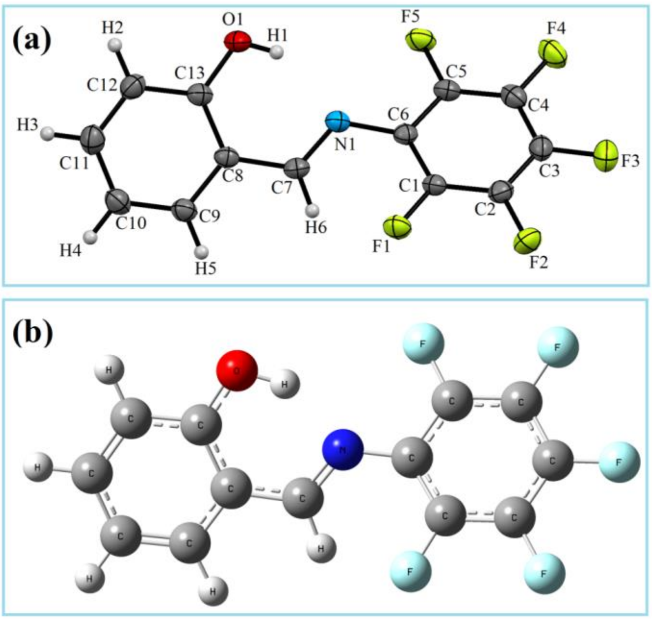

Fig. 1 Crystal structure of $C_{26}H_{12}F_{10}N_2O_2$, (a) X-ray, (b) DFT.

Table 1. Hydrogen bond geometry.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.82	1.90	2.621 (2)	146.9
C7—H6···F5^{i}	0.93	2.58	3.485 (2)	164.9
Symmetry code		(i) *x*, −*y*+3/2, *z*−1/2		

III. RESULTS AND DISCUSSION

A. The Crystal Structure of $C_{26}H_{12}F_{10}N_2O_2$

Fig. 1 depicts the asymmetric unit of the compound. The molecule is not planar because the dihedral angle of the pentafluorobenzene and the phenol rings 40.14 (5)°. The molecules are linked by intermolecular C7−H6···F5 hydrogen bond (Table 1). The compound exhibiting the S6 ring motif with O1−H1···N1 intramolecular hydrogen bond exists in the enol tautomeric form. There are also weak π···π interactions in the compound forming a three-dimensional structure in the *ac* plane and along the *b* axis. The experimental details are given in Table 2. The bond length of the hydroxyl (C−O) group in the structure was determined as 1.344(2) Å. However, the bond lengths for the C−N groups in the molecular centres N1−C6 and N1−C7 observed between the pentafluoro-benzene ring and the phenol ring for the studied molecule were determined as 1.406(3) and 1.279(3) Å, respectively.

Table 2. Experimental details of $C_{26}H_{12}F_{10}N_2O_2$.

Chemical formula	$C_{26}H_{12}F_{10}N_2O_2$
Mr	574.38
Temperature	296(2)
Wavelength	0.71073
Crystal System, Space Group	Monoclinic, $P2_1/c$
a, b, c (Å)	12.1048(10); 7.3995(4); 12.8768(10)
α, β, γ	90, 95.852 (6), 90
Cell Volume, V	1147.36 (14)
Radiation type	Mo K\a
μ (mm^{-1})	0.16
Diffractometer	STOE IPDS 2 Diffractometer
Absorption correction	integration
F(000)	576
Crystal Size	0.71 x 0.60 x 0.48
Z	2
Theta range for data collection	3.2-26
Limiting Indices	$-14 \leq h \leq 14$, $-8 \leq k \leq 9$, $-15 \leq l \leq 15$
R_{int}	0.036
wR(F^2), S	0.107, 1.05
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/Å^3)	0.12, −0.15

B. The Hirshfeld Surface Analysis

The red spots observed on the Hirshfeld surface (d_{norm}) give information about the bond strengths according to the color concentration; the dark red spots show stronger hydrogen bonds than the light red spots.

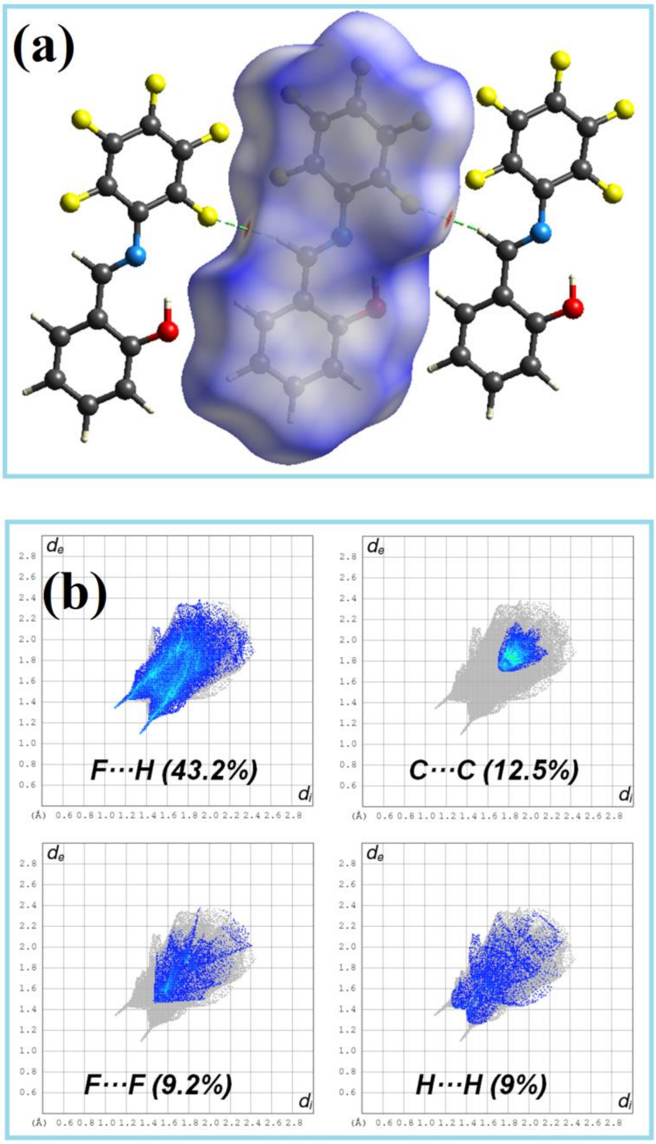

Fig. 2 (a) Hirshfeld surface and, (b) two-dimensional fingerprint of $C_{26}H_{12}F_{10}N_2O_2$.

When the red regions in the d_{norm} map showing the intermolecular contact areas of the compound in Fig. 2(a) are examined, it has been determined that they are prominent around the fluor and hydrogen atoms participating in the C−H···F contacts. The most important interaction is estimated as F···H (43.2%) interactions consisting of the appearance of the deep red color and the association with C−H···F (Fig. 2(b)). Interaction energy calculations also have close evidence as in crystal analysis. These calculations also have similar kinds of C−H···F interactions in the molecular structure.

C. *The Frontier Orbitals*

The frontier orbitals play an important role in determining both the electronic and optical properties of a molecule, especially in chemical reactions. HOMO and LUMO surfaces and energies are given in Fig. 3(a). The HOMO-LUMO band gap, that is, the difference between HOMO and LUMO energies, is an important stability index. HOMO energy is directly related to the ionization potential and LUMO energy is directly related to electron affinity. A large HOMO-LUMO gap indicates the high stability of the molecule. In this study, the ΔE value of the compound was calculated as 3.94 eV. This calculated energy gap value shows us the high kinetic value of the molecule. It shows stability and low chemical reactivity.

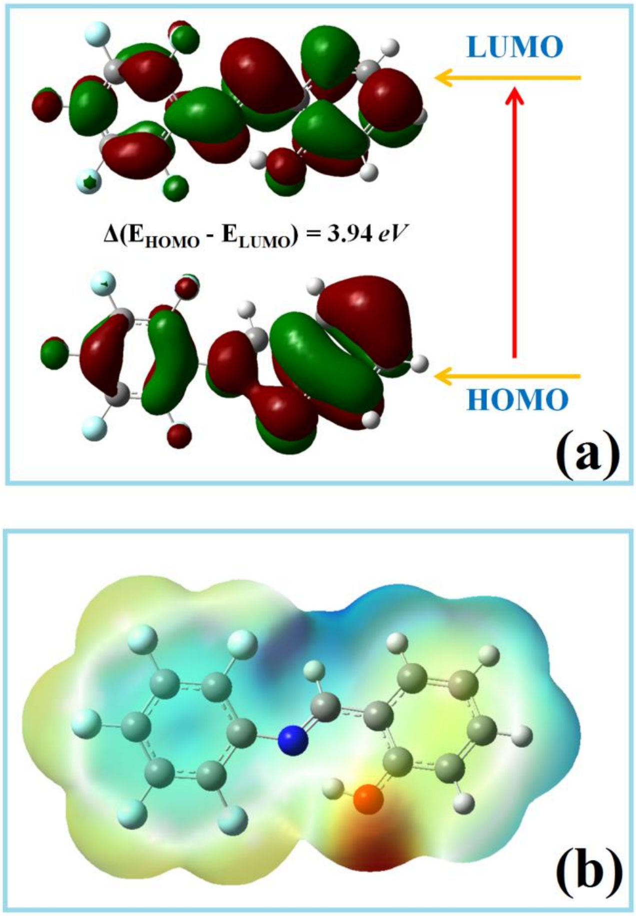

Fig. 3 (a) The energy gap and, (b) MEP map of $C_{26}H_{12}F_{10}N_2O_2$.

D. *The Molecular Electrostatic Potentials*

The molecular electrostatic potential can be defined as the interaction energy between the charge distribution of the molecular system and the positive unit charge. On the MEP map, the most negative potential is shown in red, while the most positive potential is shown in blue. MEP of molecules plays a crucial role in molecular interaction. The region where the MEP of a molecule is most negative is the region most prone to electrophilic attack; the region where it is most positive can be defined as the region most prone to nucleophilic attack. In the MEP map of the molecule, the most negative region is the electrophilic attack of this region, which is localized on the hydroxyl group oxygen, and it is the most prone region (Fig. 3(b)). On the other hand, the most positive region is located around hydrogen atoms. And this region is the most prone region to any nucleophilic attack.

IV. CONCLUSION

In this study, the structural and molecular properties of [(pentafluoro-benzylidene)amino] phenol compound were investigated by X-ray diffraction method, electronic properties were investigated by the DFT method and intermolecular interactions were investigated by Hirshfeld surface analysis. The hydrogen atoms are the most suitable regions for nucleophilic attack, and the oxygen atom is the most suitable regions for any electrophilic attack. The HOMO−LUMO energy gap was calculated as 3.94 eV, and it shows high kinetic stability and low chemical reactivity. Hirshfeld surface analysis and fingerprint plots also proved the presence of different weak intermolecular interactions, which also stabilizes and strengthens the crystal packing structure of compound.

REFERENCES

[1] N. Elangovan, R. Thomas, and S. Sowrirajan, “Synthesis of Schiff base (E)-4-((2-hydroxy-3,5-diiodobenzylidene)amino)-N-thiazole-2-yl)benzene sulfonamide with antimicrobial potential, structural features, experimental biological screening and quantum mechanical studies,” *J. Mol. Struct.*, vol. 1250, 131762, 2022.

[2] J. Ceramella, D. Iacopetta, A. Catalano, F. Cirillo, R. Lappano, and M. S. Sinicropi, “A Review on the Antimicrobial Activity of Schiff Bases: Data Collection and Recent Studies,” *Antibiotics*, vol. 11(2), pp. 191, 2022.

[3] K. D. Katariya, K. J. Nakum, and M. Hagar, “New fluorinated azo/schiff base liquid crystals: synthesis, characterisation, mesomorphic study and DFT calculations,” *Liq. Cryst.*, vol. 49(3), pp. 312-326, 2022.

[4] R. K. Mohapatra, P. K. Das, M. K. Pradhan, A. A. Maihub, and M. M. El-ajaily, “Biological aspects of Schiff base–metal complexes derived from benzaldehydes: an overview,” *J. Iran. Chem. Soc.*, vol. 15, pp. 2193–2227, 2018.

[5] T. H. Al-Noor, R. K. Mohapatra, M. Azam, L. K. A. Karim, P. K. Mohapatra, A. A. Ibrahim, P. K. Parhi, G. C. Dash, M. M. El-ajaily, S. I. Al-Resayes, M. K. Raval, and L. Pintilie, “Mixed-ligand complexes of ampicillin derived Schiff base ligand and Nicotinamide: synthesis, physico-chemical studies, DFT calculation, antibacterial study and molecular docking analysis,” *J. Mol. Struct.*, vol. 1229, 129832, 2021.

[6] M. Azam, P. K. Sahoo, R. K. Mohapatra, M. Kumar, A. Ansari, I. S. Moon, A. Chutia, S. I. Al-Resayes, and S. K. Biswal, “Structural investigations, Hirsfeld surface analyses, and molecular docking studies of a phenoxo-bridged binuclear Zinc(II) complex,” *J. Mol. Struct.*, vol. 1251, 132039, 2022.

[7] A. Mobinikhaledi, N. Foroughifar, and M. Kalhor, “Synthesis, characterization, DNA binding and nuclease activity of binuclear copper(II) complexes of semialdehyde this semi carbazones,” *Turk. J. Chem.*, vol. 34, pp. 367–373, 2010.

[8] M. M. El-ajaily, A. K. Sarangi, R. K. Mohapatra, S. S. Hassan, R. N. Eldaghare, P. K. Mohapatra, M. K. Raval, D. Das, A. Mahal, A. Cipurkovic, and T. H. Al-Noor, “Transition metal complexes of (E)-2((2-hydroxybenzylidene) amino-3-mercaptopropanoic acid: XRD, anticancer, molecular modeling and molecular docking studies,” *ChemistrySelect*, vol. 4, pp. 9999–10005, 2019.

[9] C. Stoe, X-AREA and X-RED32, Stoe & Cie, Darmstadt, Germany (2002).

[10] G. M. Sheldrick, “SHELXT-Integrated space-group and crystal-structure determination,” *Acta Crystallogr. A: Found. Adv.*, vol. 71, pp. 3−8, 2015.

[11] G. M. Sheldrick, “Crystal structure refinement with SHELXL,” *Acta Crystallogr. C: Struct. Chem.*, vol. 71, pp. 3−8, 2015.

[12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, Revision D. 01, Wallingford, CT 201, Gaussian. Inch, 2009.

[13] R. Dennington II, T. Keith, and J. Millam, Gauss View, Version 4.1.2, Semichem Inc, Shawnee Mission, KS, 2007.

[14] M. A. Spackman, and P. G. Byrom, “A novel definition of a molecule in a crystal,” *Chem. Phys. Lett.*, vol. 267, pp. 215−220, 1997.

[15] M. J. Turner, J. J. MacKinnon, S. K. Wolff, D. J. Grimwood, P. R. Spackman, D. Jayatilaka, and M. A. Spackman, *Crystal Explorer Ver. 17.5*. University of Western Australia, 2017. http://hirshfeldsurface.net.