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Crystal structure and computational studies of *N*-((2-ethoxynaphthalen-1-yl)methylene)-4-fluoroaniline

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ABSTRACT

The Schiff base compound, *N*-((2-ethoxynaphthalen-1-yl)methylene)-4-fluoroaniline, has been synthesized and characterized by X-ray diffraction method. The title compound, $C_{19}H_{16}FNO$, crystallizes in triclinic, space group *P*-1 (no. 2), a = 10.6343(9) Å, b = 11.4720(10) Å, c = 13.8297(13) Å, α = 102.466(7)°, β = 104.763(7)°, γ = 98.972(7)°, V = 1552.7(2) Å^3, Z = 4, T = 293(2) K, μ(MoKα) = 0.086 mm^{-1}, *Dcalc* = 1.255 g/cm^3, 24355 reflections measured (3.16° ≤ 2Θ ≤ 51°), 5779 unique (R_{int} = 0.0794, R_{sigma} = 0.0696) which were used in all calculations. The final R_1 was 0.0373 (I > 2σ(I)) and wR_2 was 0.0763 (all data). The title compound contains two molecules with a similar structure in the asymmetric unit cell. The packing of the crystal structure is determined by weak C–H···F and C-H···N intermolecular hydrogen bonds. The contributions of these weak interactions in the crystal structure were calculated by the Hirshfeld surfaces and examined by the intermolecular interactions within the structure. The existence, nature and percentage contribution of different intermolecular interactions H···H, C···H, N···H, and F···H were determined using Hirshfeld surface analysis and fingerprint plots.

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1. Introduction

The general formula of Schiff bases, which are compounds bearing imine groups, are RCH=NR'. They are formed as a result of condensation of aldehydes and ketones with primary amines. These compounds, discovered by Hugo Schiff, are prepared by condensing an aldehyde or a carbonyl compound with an amine group in different solvents and which are the most familiar, classical method.

Numerous spectroscopic and crystallographic studies have been carried out to explain the structure of Schiff bases in detail. In particular, *o*-hydroxy Schiff bases, which form intramolecular hydrogen bonds and have different tautomeric structures, are of great interest. *o*-.hydroxy Schiff bases generally exist in two possible tautomeric forms [1-4]. In addition, carbon-nitrogen double bonds in Schiff base compounds have played an important role in the advancement of chemistry. The important use of Schiff bases is as a starting material in the synthesis of drugs produced in pharmacology [5,6]. Naphthalene-containing Schiff bases also synthesized with two benzene rings fused to each other do not contain heteroatoms or carry substituents. They are also called benzenoid polycyclic aromatic hydrocarbons [7]. Currently, Schiff bases are being investigated as free radical scavengers that can be developed as potential antioxidants. Extending free radical delocalization of imino groups and substituent is due to the free radical scavenging effects of Schiff bases [8-10]. In this study, we have presented the synthesis and crystal structure analysis of a novel Schiff base compound, *N*-((2-ethoxynaphthalen-1-yl)methyle ne)-4-fluoroaniline which contains naphthalene used as an antioxidant. Furthermore, Hirshfeld surface analysis and fingerprint plots were used to establish the presence, nature, and percentage contribution of the different types of intermolecular interactions in the crystal.

2. Experimental

2.1 Instrumentation

X-ray diffraction data of the examined structure were collected using the STOE IPDS-II diffractometer and MoKα (λ = 0.71073 Å) beam in the X-ray Laboratory of the Faculty of Arts and Sciences, Ondokuz Mayıs University. The structure solution of the crystals was obtained using direct methods with the program SHELXS-97 [11,12].

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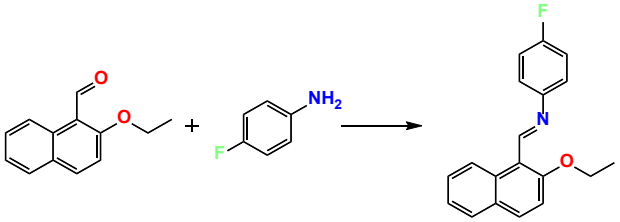
Table 1. Crystallographic characteristics and X-ray data collection and structure-refinement parameters for the title compound.

Empirical formula	$C_{19}H_{16}FNO$
Formula weight	293.33
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	*P*-1
a, (Å)	10.6343(9)
b, (Å)	11.4720(10)
c, (Å)	13.8297(13)
α (°)	102.466(7)
β (°)	104.763(7)
γ (°)	98.972(7)
Volume (Å^3)	1552.7(2)
Z	4
ρ_{calc} (g/cm^3)	1.255
μ (mm^{-1})	0.086
F(000)	616.0
Crystal size (mm^3)	0.61 × 0.38 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection (°)	3.16 to 51
Index ranges	$-12 \le h \le 12$, $-13 \le k \le 13$, $-16 \le l \le 16$
Reflections collected	24355
Independent reflections	5779 [R_{int} = 0.0794, R_{sigma} = 0.0696]
Data/restraints/parameters	5779/40/515
Goodness-of-fit on F^2	0.789
Final R indexes [I≥2σ (I)]	R_1 = 0.0373, wR_2 = 0.0656
Final R indexes [all data]	R_1 = 0.0975, wR_2 = 0.0763
Largest diff. peak/hole (e.Å^{-3})	0.09/-0.12
CCDC no	2100901
Programs	SHELXL97 [11,12], X-AREA [13], X-RED32 [13], ORTEP-3 [14], WinGX [14], PLATON [15]



Scheme 1. Synthesis of the title compound.

In the solution phase, refinement was carried out with the program SHELXL-97 [11,12], which uses the full matrix least squares method to determine the positions of atoms other than hydrogen. In the first stage of the purification, isotropic purification was performed to make the atom positions more sensitive and to identify the missing atoms. As a result of the purification, it was observed that there were no missing atoms except hydrogen and anisotropic purification was carried out. The melting point of the compound was measured with the Gallenkamp melting point apparatus. The synthesized solid form crystal was crushed into powder and formed into a disc with KBr, and FT-IR spectra were recorded in the range of 400-4000 cm^{-1} with Bruker Vertex 80V FT-IR spectrometer (Ondokuz Mayıs University).

2.2. Synthesis

2-Ethoxy-1-naphthaldehyde and 4-fluoroaniline were obtained from Acros Organic and Aldrich Chemical Companies. *N*-((2-Ethoxynaphthalen-1-yl)methylene)-4-fluoroaniline was prepared by refluxing at 350 K of a mixture of a solution containing 2-ethoxy-1-naphthaldehyde (20.0 mg, 0.1 mmol) in ethanol (20 mL) and a solution containing 4-fluoroaniline (11.1 mg, 0.1 mmol) in ethanol (20 mL) (Scheme 1). The prepared mixture was stirred for 5 hours to react. Crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of an ethanol solution of the title compound at room temperature for 3 days. Yield: 68%. M.p.: 75-79 °C. FTIR (KBr, ν, cm^{-1}): 3520, 2980, 1702, 1676, 1625, 1523, 1446, 1370.

3. Results and discussion

In this study, single crystal X-ray diffraction method was used to determine the molecular structure of *N*-((2-ethoxynaphthalen-1-yl)methylene)-4-fluoroaniline compound (Figure 1). The crystallographic characteristics and the X-ray data collection and structure refinement parameters for the title compound are given in Table 1. The obtained geometrical parameters are given in Tables 2 and 3.

The CN group in the molecule, the C=N double bond, has a strong electron-withdrawing effect. The presence of the C=N double bond in the molecule indicates that the enol-imine is in the tautomeric form [16]. The lengths of the C=N bonds in molecule A and B were measured as 1.265 (2) Å. The presence of single C-O bonds in the molecule also shows that the tautomer structure contains an imine form. The C-O bond (C17-O1 and C18-O1) lengths in molecules A and B were measured as 1.369(2), 1.428(2) and 1.360(2), 1.430(3) Å, respectively. The details obtained are compatible with similar structures reported in the literature [17,18].

Torsion angles τ1(N1A-C7A-C8A-C9A) and τ2(C3A-C4A-N1A-C7A) correspond to the tautomeric equivalents of the groups and these values are 19.2(3) and -134.38(18)°, respectively. These values show that the structure is not planar [19].

The packing of the crystal structure in the title compound is stabilized by intermolecular C-H···N, C-H···F hydrogen bonds and π-π stacking interactions (Figure 2). The molecular structure of the title compound contains intermolecular C-H···N and C-H···F hydrogen bonds (Table 4).

Table 2. Bond lengths for the title compound.

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)	Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
C1A	C2A	1.361(3)	C4B	C5B	1.373(2)	C9A	C10A	1.419(3)	C14A	C15A	1.405(3)
C1A	C6A	1.352(3)	C4B	N1B	1.423(2)	C9A	C14A	1.418(2)	C14B	C15B	1.398(3)
C1A	F1A	1.368(2)	C5A	C6A	1.378(3)	C9B	C10B	1.404(3)	C15A	C16A	1.347(3)
C1B	C2B	1.351(3)	C5B	C6B	1.377(2)	C9B	C14B	1.429(2)	C15B	C16B	1.335(3)
C1B	C6B	1.354(2)	C7A	C8A	1.459(2)	C10A	C11A	1.364(3)	C16A	C17A	1.407(3)
C1B	F1B	1.3667(18)	C7A	N1A	1.265(2)	C10B	C11B	1.360(3)	C16B	C17B	1.432(3)
C2A	C3A	1.379(3)	C7B	C8B	1.470(2)	C11A	C12A	1.396(4)	C17A	O1A	1.369(2)
C2B	C3B	1.374(3)	C7B	N1B	1.265(2)	C11B	C12B	1.395(3)	C17B	O1B	1.360(2)
C3A	C4A	1.385(2)	C8A	C9A	1.429(2)	C12A	C13A	1.337(3)	C18A	C19A	1.481(3)
C3B	C4B	1.380(2)	C8A	C17A	1.389(2)	C12B	C13B	1.342(3)	C18A	O1A	1.428(2)
C4A	C5A	1.381(2)	C8B	C9B	1.426(2)	C13A	C14A	1.416(3)	C18B	C19B	1.481(4)
C4A	N1A	1.415(2)	C8B	C17B	1.378(3)	C13B	C14B	1.412(3)	C18B	O1B	1.430(3)

Table 3. Bond angles for the title compound.

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
C2A	C1A	F1A	117.9(2)	C10B	C9B	C8B	124.26(17)	C16A	C15A	C14A	122.4(2)
C6A	C1A	C2A	123.2(2)	C10B	C9B	C14B	116.51(19)	C16B	C15B	C14B	122.8(2)
C6A	C1A	F1A	118.9(2)	C11A	C10A	C9A	120.6(2)	C15A	C16A	C17A	119.3(2)
C2B	C1B	C6B	122.84(18)	C11B	C10B	C9B	122.3(2)	C15B	C16B	C17B	119.3(2)
C2B	C1B	F1B	118.83(17)	C10A	C11A	C12A	121.5(3)	C8A	C17A	C16A	121.7(2)
C6B	C1B	F1B	118.32(18)	C10B	C11B	C12B	120.6(3)	O1A	C17A	C8A	116.31(16)
C1A	C2A	C3A	118.3(2)	C13A	C12A	C11A	119.6(3)	O1A	C17A	C16A	121.96(18)
C1B	C2B	C3B	118.49(19)	C13B	C12B	C11B	119.4(3)	C8B	C17B	C16B	120.9(2)
C2A	C3A	C4A	120.3(2)	C12A	C13A	C14A	121.3(3)	O1B	C17B	C8B	116.39(19)
C2B	C3B	C4B	120.8(2)	C12B	C13B	C14B	121.8(2)	O1B	C17B	C16B	122.6(2)
C3A	C4A	N1A	118.62(17)	C13A	C14A	C9A	119.9(2)	O1A	C18A	C19A	107.94(19)
C5A	C4A	C3A	119.16(18)	C15A	C14A	C9A	118.7(2)	O1B	C18B	C19B	107.1(3)
C5A	C4A	N1A	122.20(17)	C15A	C14A	C13A	121.4(2)	C7A	N1A	C4A	117.81(16)
C3B	C4B	N1B	123.33(17)	C13B	C14B	C9B	119.3(2)	C7B	N1B	C4B	118.31(15)
C5B	C4B	C3B	118.71(17)	C15B	C14B	C9B	118.6(2)	C17A	O1A	C18A	120.06(15)
C5B	C4B	N1B	117.92(15)	C15B	C14B	C13B	122.1(2)	C17B	O1B	C18B	120.4(2)
C6A	C5A	C4A	120.5(2)	C17B	C8B	C9B	119.09(18)	N1B	C7B	C8B	124.82(18)
C4B	C5B	C6B	120.77(18)	C10A	C9A	C8A	123.41(18)	C9A	C8A	C7A	124.60(17)
C1A	C6A	C5A	118.5(2)	C14A	C9A	C8A	119.53(17)	C17A	C8A	C7A	116.97(18)
C1B	C6B	C5B	118.39(19)	C14A	C9A	C10A	117.1(2)	C17A	C8A	C9A	118.41(16)
N1A	C7A	C8A	126.4(2)	C8B	C9B	C14B	119.23(19)	C9B	C8B	C7B	124.38(18)

Table 4. Hydrogen bonds for the title compound.

D	H	A	d(D-H) (Å)	d(H-A) (Å)	d(D-A) (Å)	∠D-H-A (°)
C18B	H18C	F1A [1]	1.00(3)	2.44(3)	3.311(4)	145(2)
C5B	H5B	N1B [2]	0.968(17)	2.639(18)	3.603(2)	174.0(13)

Symmetry codes: [1] -1+*x*, +*y*, -1+*z*; [2] -*x*, 1-*y*, -*z*.

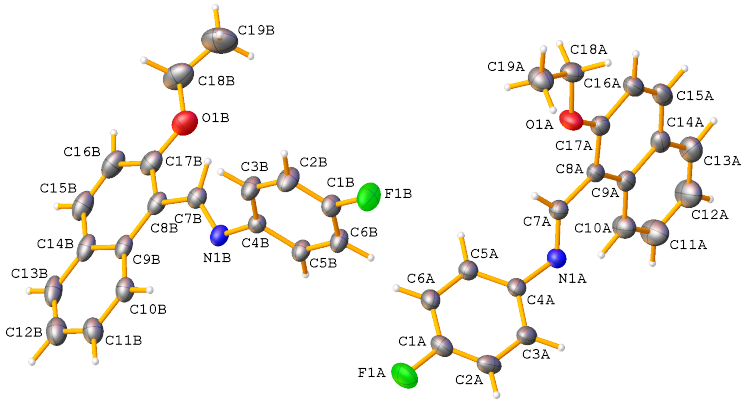


Figure 1. The molecular structure of the title compound.

In addition, there is also C-H···π stacking interactions [C6B-H6B···Cg7 (C9B-C14B) H6B···Cg7: 2.72(2) Å, symmetry code: -*x*, 1-*y*, -*z*; C11-H11B···Cg3 (C9A-C14A) H11B···Cg3: 2.96(2) Å, symmetry code: 1-*x*, 1-*y*, -*z*] and C-F···π stacking interaction [C1B-F1B···Cg1 (C1A-C6A) F1B···Cg1: 4.1209(4) Å, symmetry code: -1+*x*, *y*, -1+*z*] exist in the molecule.

3.1. Hirshfeld surface analysis

CrystalExplorer program was used for Hirshfeld surface analysis of the title molecule [20]. The d_{norm} surface is used to analyze and visualize the interactions between molecules and atoms in the studied structure. d_e and d_i distances are normalized distances. d_e is the distance from the outer surface of the nearest atom to the Van der Waals surface. d_i is the distance from the inner surface of the nearest atom. In addition, the white, blue, and red colors represented on the Hirshfeld surface in the d_{norm} map indicate that the interaction distances between atoms are equal, longer, or shorter than the Van der Waals surface [21, 22]. Figure 3 shows a 3D d_{norm} plot with normalized d_e and d_i interactions for the title compound. When the figure is examined, the bright red dots around the oxygen and hydrogen atoms represent donors and acceptors of the C-H···N interaction.

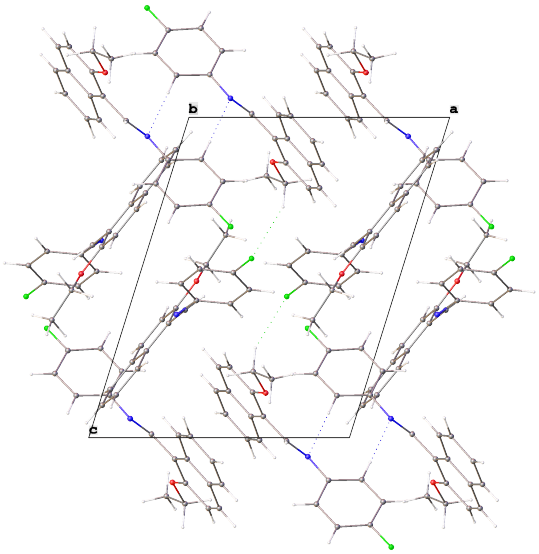


Figure 2. Packing diagram of the title compound.

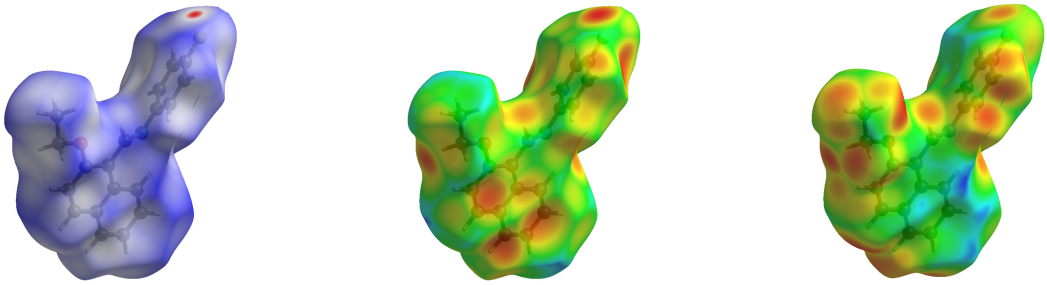


Figure 3. Three-dimensional view of the Hirshfeld surface (d_{norm}, d_e, and d_i).

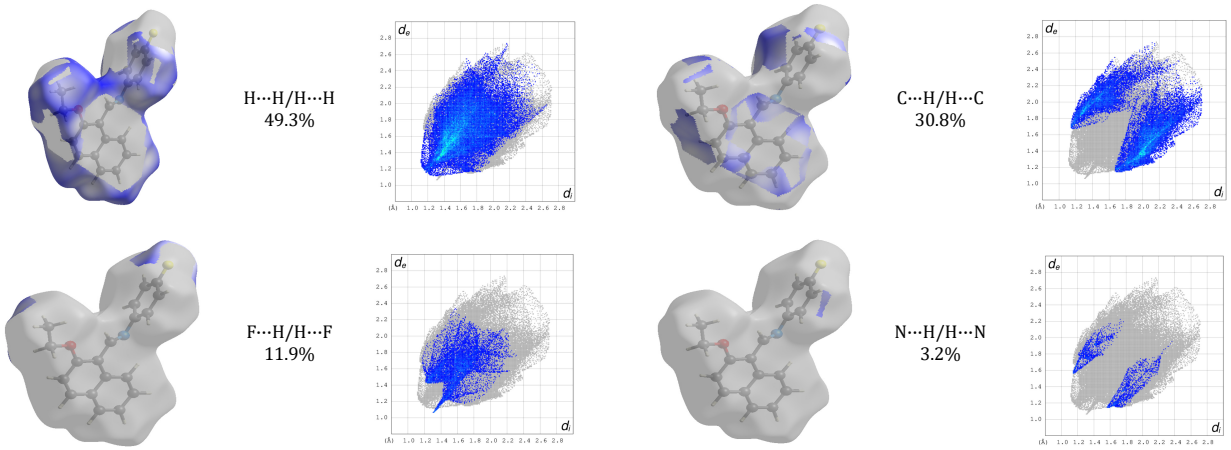


Figure 4. Contribution of crystalline atom pairs to Hirshfeld surface and two-dimensional fingerprint drawings.

In Figure 2, where two-dimensional fingerprint plots are shown (scattering points spread up to d_e = d_i = 1.5 Å), the dominant interaction of the analyzed compound originates from the H···H contacts, and these H···H contacts contribute to the Hirshfeld surface. It was calculated as 49.3%. Contribution from N···H/F···H contacts corresponding to the intermolecular interactions of C5-H5···N1 in the middle and C18-H18C··F1 at the far end (3.2% + 11.9% = 15.1%), in Figure 4. It is represented by a sharp spike formed as a pair. Other important interactions found in the molecule are C···H (30.8%) and O···H (2.5%) in percentile order. In addition, while there is a high probability that there are other identifiable contact points in the molecule that can be identified, their importance is likely to be of limited importance. Therefore, it is not be necessary to discuss or explain it in detail in this study [23,24].

4. Conclusions

A Schiff base compound, *N*-((2-ethoxynaphthalen-1-yl) methylene)-4-fluoroaniline, was synthesized by reacting 2-ethoxy-1-naphthaldehyde and 4-fluoroaniline. The structure of the compound was confirmed by X-ray crystallography.

Compound that crystallizes in imine form in the triclinic *P*-1 Bravais lattice. C–H···F and C-H···N intermolecular hydrogen bonds determine the packing of the crystal structure. In the Hirshfeld calculations within the structure, the percentages of H···H, C···H, F···H, and N···H interactions were calculated as 49.3, 30.8, 11.9, and 3.2%, respectively.

Supporting information

CCDC-2100901 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif, or by e-mailing data request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Author contributions: All authors contributed equally to this work.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

CRediT authorship contribution statement

Conceptualization: Hakan Bulbul, Sehriman Atalay; Software: Hakan Bulbul, Sehriman Atalay; Validation: Sehriman Atalay; Formal Analysis: Mustafa Macit; Investigation: Sehriman Atalay; Resources: Mustafa Macit; Data Curation: Hakan Bulbul; Writing - Original Draft: Sehriman Atalay; Writing - Review and Editing: Hakan Bulbul; Visualization: Hakan Bulbul; Funding acquisition: Mustafa Macit; Supervision: Mustafa Macit; Project Administration: Mustafa Macit.

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