

**CRYSTAL, MOLECULAR AND ELECTRONIC PROPERTIES
OF (E)-1-((5'-BROMO-[2,2'-BITHIOPHEN]-5-YL)METHYLENE)-2-
(PENTAFLUOROPHENYL)HYDRAZINE**

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Abstract. The pentafluorophenyl group is an important constituent not only in biological chemistry, but also in analytical, material and polymer chemistry, catalysis, dynamic combinatorial chemistry, and reaction development. We reported here the structures of new Schiff base 1-((5'-bromo-[2,2'-bithiophen]-5-yl)methylene)-2-(pentafluorophenyl) hydrazine (**I**), C₁₅H₆BrF₅N₂S₂, which crystallizes as racemate in the space group P-1. The C—S, C—F and the N—H bonds are presented. The dihedral angle between the thiophene rings is 3.33 (0.19)° and the side ring (C1 to C6) is 9.29 (18) and 10.73 (18)°, respectively. The crystal structure is slightly stabilized by the intramolecular N—H···F and intermolecular N—H···F, C—H···F hydrogen bonds as H-atoms donor, link the molecules into dimers along the *b* axis. Calculations of the NBO analyses (DFT/B3LYP/cc-pVDZ, single point geometry) were performed.

Keywords: crystal structure, DFT/B3LYP/cc-pVDZ, hydrazine, *R* factor, single crystal, T = 298 K, X-ray diffraction, *wR* factor

Mathematics Subject Classification: 74E15; 37N20

1 Comments

The pentafluorophenyl group is an important constituent not only in biological chemistry, but also in analytical, material and polymer chemistry, catalysis, dynamic combinatorial chemistry, and reaction development. Despite this widespread interest, as part of our studies on the substituent effects on the structures containing pentafluorophenyl group and 5'-bromo-[2,2'-bithiophen]-5-yl)methylene fragment we investigated the hitherto not prepared Schiff base 1-((5'-bromo-[2,2'-bithiophen]-5-yl)methylene)-2-(pentafluorophenyl)hydrazine (**I**) is known to exhibit a wide variety of activities. We report here the crystal, molecular structure and electronic properties of the title compound (Fig. 1).

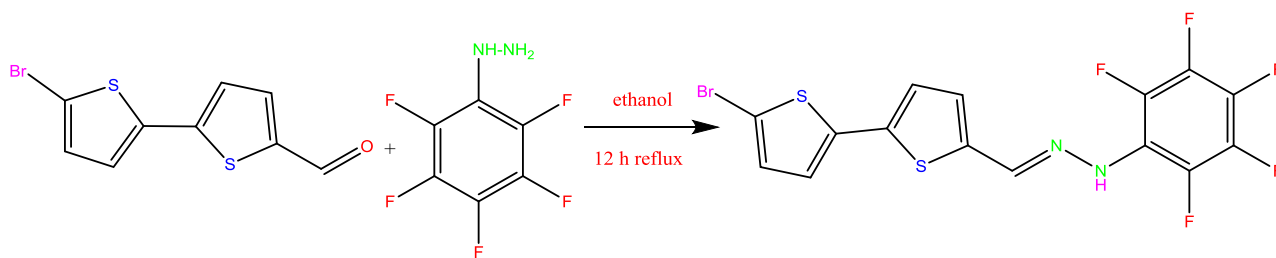


Fig. 1. Synthesis of (*E*)-1-((5'-bromo-[2,2'-bithiophen]-5-yl)methylene)-2-(pentafluorophenyl)hydrazine.

2 Experimental

The reaction of pentafluorophenylhydrazine with 5'-bromo-(2,2'-bithiophene)-5-carbaldehyde in ethanol gave the desired Schiff base 1-((5'-bromo-[2,2'-bithiophen]-5-yl)methylene)-2-(pentafluorophenyl)hydrazine with high yield and purity were characterized by elemental analyses, spectroscopic methods and X-ray diffraction analyses [1, 2, 3]. According to the reaction scheme (Fig. 1), the corresponding aldehyde (0.01 mol) was dissolved in 60 ml ethanol which contained solution of 0.011 mol pentafluorophenylhydrazine. The reaction mixture was refluxed for 12 h with the addition of 2 drops of concentrated HCl. The solvent was evaporated and the obtained crude product was purified by column chromatography to give the pure product in 68% yield. M.p. 149-151 °C.

¹H NMR (300 MHz, dmsO) δ 10.37 (s, 1H), 8.22 (s, 1H), 7.20 (m, 4H).

¹³C NMR (75 MHz, dmsO) δ 139.11, 138.06, 137.62(m), 137.21(m), 136.71, 135.48, 133.71(m), 131.67, 129.16, 125.02, 124.73, 120.87 (m), 110.67.

¹⁹F NMR (282 MHz, dmsO) δ -155.69 (2F, d, *J* = 24.0 Hz), -164.35 (2F, td, *J* = 21.6, 2.7 Hz), -169.87 (1F, tt, *J* = 23.3, 5.7 Hz).

2.1 Refinement

Hydrogen atoms were placed in calculated positions with C—H distances of 0.93 Å and constrained to ride on their parent atoms. The amide H atom was visible in a difference map and refined with the N—H distance restrained to 0.86 (2) Å. The *U*_{iso}(H) values were set at 1.2*U*_{eq}. Friedel pairs were merged. Refinement on *F*², least-squares matrix: full, *R*[*F*² > 2σ(*F*²)] = 0.039, *wR*(*F*²) = 0.090, *S* = 1.03, 3921 reflections, 226 parameters, 0 restraint, primary atom site location: structure-invariant direct methods, secondary atom site location: difference Fourier map, Hydrogen site location: inferred from neighbouring sites, H atoms treated by a mixture of independent and constrained refinement, Δρ_{max} = 0.28 eÅ⁻³, Δρ_{min} = -0.32 eÅ⁻³, Triclinic, P-1, *a* = 6.2562 (3), *b* = 9.0987 (8), *c* = 14.7830 (12) (Å), α = 102.555 (8), β = 93.116 (6), γ = 101.968 (7) (°).

2.1.1 Computing details

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS* [9], *Sir2014* ([5]; program(s) used to refine structure: *SHELXL* [9]; molecular

graphics: *DIAMOND* [4]; software used to prepare material for publication: *SHELXL* [9], *ShelXle* [8], *PLATON* [10], *OLEX2* [6], *Gaussian 09* [7].

3 Results

We present here the crystal, molecular and electronic structure of one novel (*E*)-1-((5'-bromo-[2,2'-bithiophen]-5-yl)methylene)-2-(pentafluorophenyl)hydrazine (**I**). Compound (**I**) crystallizes in triclinic system, centrosymmetric space group *P*-1. The dihedral angle between the thiophene rings is 3.33 (0.19)° and the side ring (C1 to C6, pentafluorophenyl) is 9.29 (18) and 10.73 (18)°, respectively. Crystallographic data for the structure reported in this paper will be available from the Cambridge Crystallographic Data Centre. The hydrogen atom of the NH is involved in intramolecular hydrogen bonding and intermolecular hydrogen bonding. The crystal structure is stabilized by the intramolecular N2—H2···F1 bond and two intermolecular N2—H2···F1ⁱ, F1···H2—N2ⁱ hydrogen interactions as H-atoms donor, link the molecules into dimers along the *b* axis, we also see intermolecular C13—H13···F3ⁱⁱ and C13—H13···F4ⁱⁱ hydrogen interactions (Figs. 2, 3 and Tab. 1). Table 3 shows us the distance between ring centroids (Å) of Cg(1) (S1-C8-C11-C10-C9, Cg(2) (S2-C12-C13-C14-C15, Cg(3) (C1-C2-C3-C4-C5-C6). The bond lengths of the hydrazine group N1=C7 is 1.274 (4) Å somewhat shorter than typical bond [1]. This may be due to the fact that C7H7 is not participate in intra- and intermolecular hydrogen bonds. Atom N2 is *sp*²-hybridized, as evidenced by the sum of the valence angles around it (359.99°). These data are consistent with conjugation of the lone-pair electrons on N2, similar to what is observed for amides. The electronic structure of the molecule of the title compound (**I**) was calculated by the *Ab Initio* method [7], DFT/B3LYP/cc-pVDZ basis set was involved into calculation. Calculation of the electronic structure of a compound provides several indices which characterize the distribution of electron density in the molecule and the multiplicity of atomic bonds. The selected net charges give a Tab. 2 of the distribution of electron density in the molecule and the values of the Wiberg bond indices enable one to estimate the multiplicity of individual atomic bonds. The net charge distribution in the molecule indicates that the positive charges are localized at the atoms N2 (0.049), S1 and S2 (0.159 and 0.183), whereas the negative net charges are located on the N1 (−0.100), F1 (−0.163), F2 (−0.143), F3 (−0.146), F4 (−0.143) and F5 (−0.135). This charge distribution and the spatial arrangement (geometry) of the molecule govern its activity and are important for the overall stabilization of the crystal structure. It follows from the Wiberg index value for the bond N1—C7 (*I*_w = 1.695) is not a pure double bond but indicate the character of conjugated bond. The other bonds of the molecule have the character of single bonds (Tab. 2). That π -electrons are delocalized in the region of the C1 to C6 atoms and atoms S1, S2, Br1. The results of these calculations are in good agreement with the experimental values of the bond lengths found by the X-ray structure analyses. It was found by evaluating experimental interactions of the structure (**I**) in the solid phase in this work that the intra- and intermolecular interactions are nevertheless important in the parts of the molecule (**I**), (Tab. 1, Tab. 2).

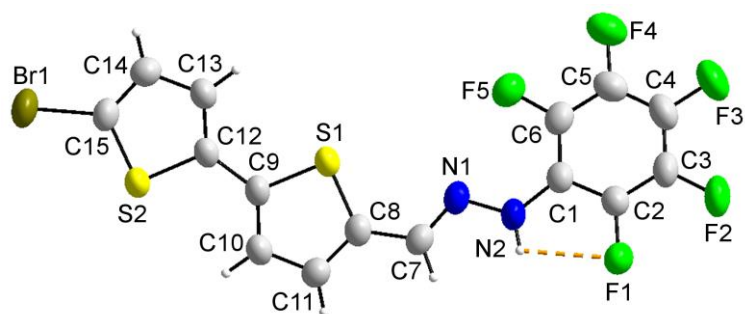


Fig. 2. Molecular structure of the title compound (**I**) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level. H atoms are represented as small spheres of arbitrary radii.

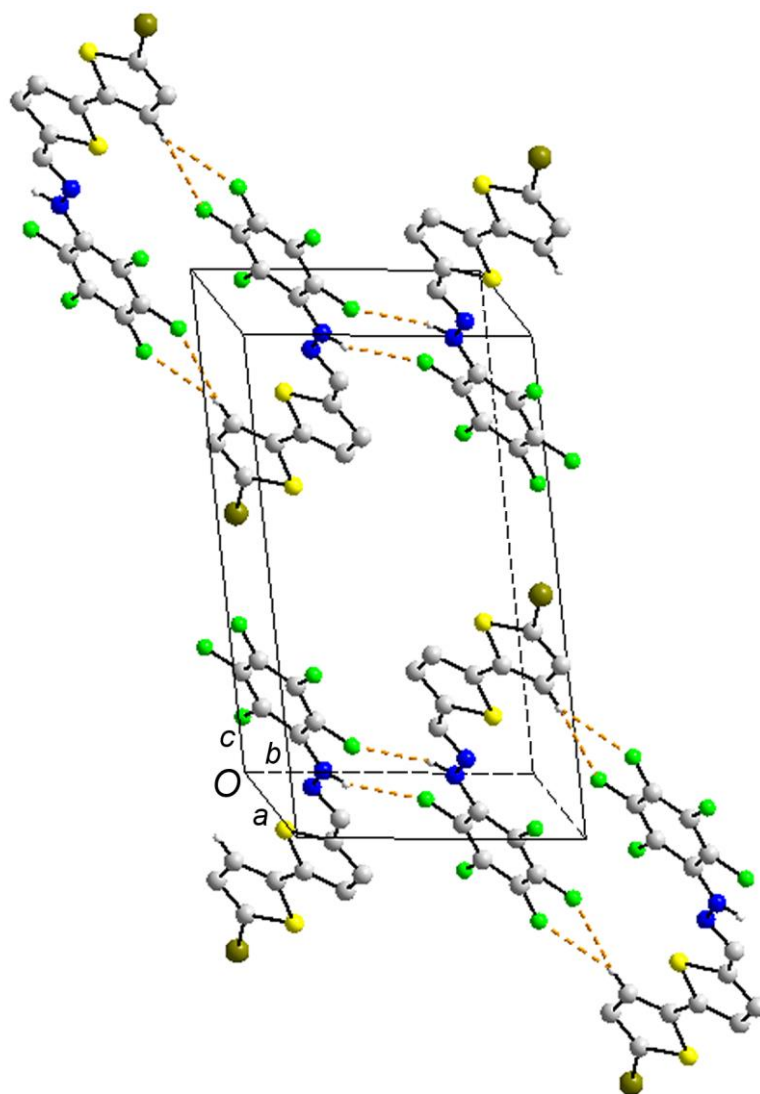


Fig. 3. Molecular packing view of the title compound (**I**). Molecular links along *c*-axis are generated by N—H · · · F, F · · · H—N hydrogen bonds which are shown by dashed lines. The rest of H atoms have been omitted for clarity.

$D-H\cdots A$	D—H	H $\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 \cdots F1	0.86	2.28	2.645(3)	106
N2—H2 \cdots F1 ⁱ	0.86	2.32	3.119(2)	155
F1 \cdots H2—N2 ⁱ	0.86	2.32	3.119(2)	155
C13—H13 \cdots F3 ⁱⁱ	0.93	2.59	3.246(3)	128
C13—H13 \cdots F4 ⁱⁱ	0.93	2.87	3.746(3)	173

Symmetry code: (i) 2-x, 1-y, 2-z; (ii) -x, -y, 2-z

Tab. 1. Hydrogen-bond geometry (Å, °) for (I).

Atoms	Charge, q	Bond	I_w	Atoms	Charge, q
N1	-0.100	N1-C7	1.695	F4	-0.143
N2	0.049	N1-N2	1.107	F5	-0.135
H2	-0.019	N2-C1	1.103	C1	0.019
Br1	0.002	Br1-C15	1.061	C7	0.255
S1	0.159	S1-C9	1.166	C8	-0.205
S2	0.183	S2-C12	1.148	C9	-0.112
F1	-0.163	F1-C2	0.876	C12	-0.122
F2	-0.143	F3-C4	0.896	C15	-0.279
F3	-0.146	F5-C6	0.902		

Tab. 2. Selected values of the net charges (NBO) at individual atoms and Wiberg bonding indices I_w .

Cg(1) - Cg(2) ⁱⁱⁱ	3.714(2)
Cg(1) - Cg(3) ^{iv}	4.046(2)
Cg(2) - Cg(1) ^v	3.714(2)
Cg(2) - Cg(2) ^{vi}	3.975(2)
Cg(3) - Cg(1) ^{iv}	4.046(2)
Cg(3) - Cg(3) ^{vii}	4.314(2)

Symmetry code: (iii) 1+x, y, z; (iv) 1-x, 1-y, 2-z; (v) -1+x, y, z;
(vi) -1-x, -y, 1-z; (vii) 1-x, -y, 2-z

Tab. 3. Distance between ring centroids (Å).

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