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Crystal interaction, XRD powder, and Hirshfeld surface analysis of S-benzyl-β-N-(1-(4-chlorophenyl) ethylidene) dithiocarbazate Schiff base

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Abstract

The reaction of S-benzyldithiocarbazate with 4-chloroacetophenone afforded bidentate NS Schiff base (S.B) S-benzyl-β-N-(1-(4-chlorophenyl)ethylidene) dithiocarbazate, the thione tautomeric is very interesting, usually such Schiff base chelated to the metal center through neutral nitrogen at in the azomethine and the ionic sulfur of the thiol. The ligand structure has been confirmed by FT-IR, FAB-MS, UV-vis, PXRD and XRD-crystal. The main target of this work is to compare the XRD-interactions with the computed result of Hirshfeld surface analysis (HSA). Both HSA and XRD reflected the presence of the NH…S=C and CH….S=C. H-bonds as main interactions forces in crystal lattice of the desired ligand.

Keywords: *PXRD, dithiocarbazate; crystal structure, Hirshfeld analysis.*

1. Introduction

Schiff Base (S.B) having nitrogen and Sulphur donor atoms have shown very interesting attention for the past century [1-2]. A wide range of biological activities has been reported using these materials such as antibacterial, antifungal anticancer, and DNA binding [3-10]. In complexes, the hydrogen bonding via the imino group with metal ion has tolerated good chelating in biological applications [10]. Interestingly, the substituted benzene ring showed Gram-positive/negative antibacterial activities dependent on the position of the substituents [9, 10]. Dithiocarbazides S. B with have good roles in metals center complexation due to the sulfur and nitrogen bidentate affinity, for this reason, it gained the confidence of chemists as a stable polychelate ligands [11]. Generally, the dithiocarbazate S.B ligands were performed by condensed thioazinde with certain carbonyl compounds like aldehydes, and ketones [12-15]. The tautomeric processes in dithiocarbazate like thione to thiol gains role in a variety of prepared coordination structures of complexes cased a naked eye colorimetric changes [11-16]. As an extension of our ongoing work, we recently developed new methods for preparing the several types of S.B and their complexes [17-25]. Herein, the S-benzyl-β-N-(1-(4-chlorophenyl)ethylidene) dithiocarbazate, the thione S. B ligand was made available then proved by PXRD and XRD-crystal. The computed HSA analysis was successfully compared to the XRD-result as they were agreed on the nature of interactions in the crystal lattice.

2. Materials and methods

2.1. Measurements

All the chemicals and solvents were of reagent grade and used without further Purification. Chemicals such as hydrazine hydrate (90%); carbon disulphide and potassium hydroxide were purchased from (Fluka-sigma) while benzyl chloride and 4-Chloroacetophenone were obtained by Manchester salt and catalysis ltd UK. Copper (II) Nitrate trihydrate were obtained from Fluka Chemica (Switzerland). UV-Vis. measurements were performed in methanol solvent using TU-1901 double-beam spectrophotometer. The FT-IR (MID. 4000-200 cm^{-1}) was recorded in solid state using PerkinElmer Spectrum 1000 FT-IR Spectrometer. MS data was carried out on a 711A (8 kV) Finnigan. CHN-analysis was measured using ElementarVarrio EL-analyzer.

2.2. Synthesis of the Schiff base S-benzyl-β-N-(1-(4-chlorophenyl) ethylidene) dithiocarbazate

The ligand precursor, S-benzyl dithiocarbazate (SBDTC) is well known was prepared by literature method [16]: SBDTC (1.98 g, 10 mmol) was dissolved in absolute ethanol (40 mL). To this solution, 4-chloroacetophenone (1.30ml, 10 mmol) in absolute ethanol (10 mL) was added and the mixture was refluxed for 4 hrs. The aliquot was cooled at room temperature. The light yellow precipitate, which formed was separated, dried, and kept in a desiccator (Yield: 2.1 g, 50 %). The product was recrystallized from absolute ethanol. Colorless needle shaped single crystals were obtained after crystallization of 0.15 g of the recrystallized product from chloroform (25 mL) and few drops of hexane over 10 days , m.p.;173 °C. CHN Calc. formula: $C_{16}H_{15}N_2S_2Cl$: C, 57.48%; H, 4.49%; N, 8.38%; S, 19.16%; Cl, 10.47%; Found: C, 56.55%; H, 4.06%; N, 7.35%; S, 18.86%; Cl, 10.11%.

2.3. Computational

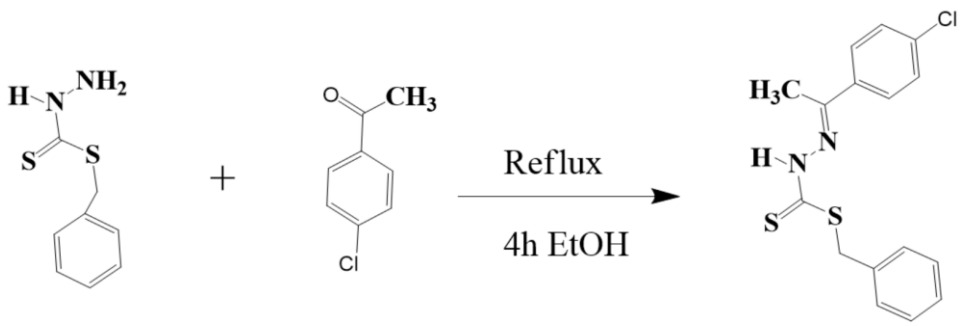
The CIF file crystallographic data was taken as reference for the calculation when HSA was performed using the CRYSTAL EXPLORER 3.1 [26].

3. Results and Discussions

3.1. Synthesis and XRD

The ligand precursor was prepared by condensation of S-benzyl dithiocarbazate with 4-chloroacetophenone following the literature method [15]. The desired ligand structure S-benzyl-β-N-(1-(4-chlorophenyl) ethylidene) dithiocarbazate

was tautomerized to (1E,1E)-benzyl hydrogen (1-(4-methoxyphenyl)ethylidene)carbono-hydrazonodithioate via single proton transfer mechanism to form the thiol ligand form [27-30].



Scheme1. Ligand synthesis.

The crystal parameters of the ligand, ORTEP and packing diagrams reported in Table 1 and Fig.1, respectively. The free desired ligand was crystallized in a is a Triclinic, system with *P* space group (Z = 2) four unit per cell. *E*-conformation as sterically favored kinetic isomer in (E)-benzyl 2-(1-(4-methoxyphenyl)-ethylidene)-hydrazinecarbodithioate was detracted (Fig.1a). The XRD showed the structure of the ligand in thione tautomeric form with S in S-Ph and N in N=C functional groups in the same ordination, meanwhile, the Ph's are in perpendicular to each other (Fig.1a). The structure packing reflected several intermolecular interactions in the crystal lattice of the ligand.

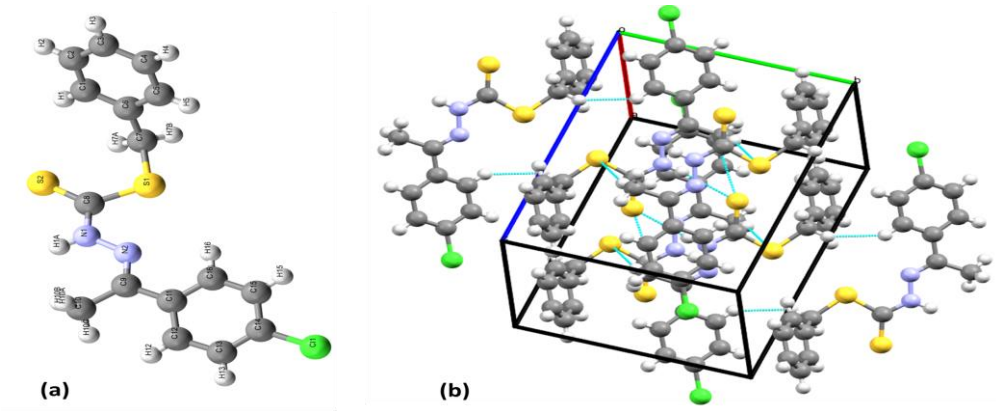


Fig.1. (a) ORTEP, and (b) total interaction packing diagrams of the ligand.

3.2. PXRD investigation

PXRD powder diffraction of the ligand was performed to support the purity and crystallinity degrees of the ligand as seen in Fig.2a. The figure reflected a high degree of purity with a triclinic crystallization system (Fig.1b).

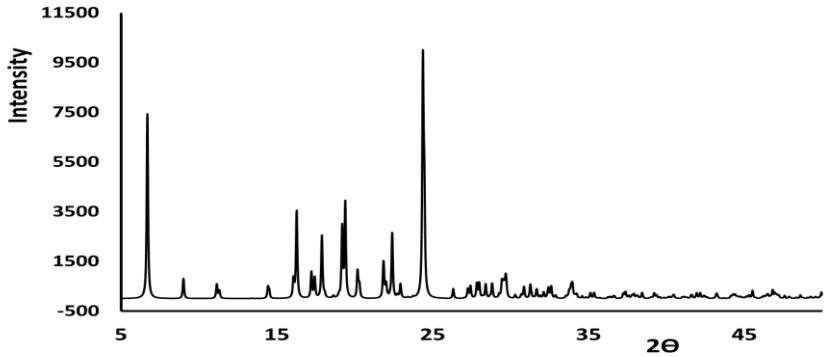


Fig.2. PXRD of the ligand.

Table 1. XRD-exp. bond lengths (Å) and angles (°).

No.	Bond		Å	No.	Angels			(°)
1	Cl1	C14	1.73(1)	1	C7	S1	C8	101.8(4)
2	S1	C7	1.827(9)	2	N2	N1	C8	121.3(7)
3	S1	C8	1.789(8)	3	C2	C1	C6	120.0(9)
4	N1	N2	1.39(1)	4	N1	N2	C9	121.4(7)
5	N1	C8	1.33(1)	5	C1	C2	C3	122(1)
6	C1	C2	1.40(1)	6	C2	C3	C4	118(1)
7	C1	C6	1.37(1)	7	C3	C4	C5	121(1)
8	S2	C8	1.65(1)	8	C4	C5	C6	120.2(9)
9	N2	C9	1.25(1)	9	C1	C6	C5	118.7(8)
10	C2	C3	1.33(2)	10	C1	C6	C7	120.9(8)
11	C3	C4	1.36(2)	11	C5	C6	C7	120.2(8)
12	C4	C5	1.40(1)	12	S1	C7	C6	115.5(6)
13	C5	C6	1.34(1)	13	S1	C8	N1	110.9(6)
14	C6	C7	1.47(1)	14	S1	C8	S2	124.9(5)
15	C9	C10	1.50(1)	15	N1	C8	S2	124.3(6)
16	C9	C11	1.46(1)	16	N2	C9	C10	123.5(7)
17	C11	C12	1.39(1)	17	N2	C9	C11	116.6(7)
18	C11	C16	1.39(1)	18	C10	C9	C11	120.0(7)
19	C12	C13	1.40(2)	19	C9	C11	C12	122.4(7)
20	C13	C14	1.35(1)	20	C9	C11	C16	121.5(7)
21	C14	C15	1.37(1)	21	C12	C11	C16	116.2(8)
22	C15	C16	1.40(2)	22	C11	C12	C13	120.3(9)
				23	C12	C13	C14	122.6(9)
				24	Cl1	C14	C13	122.1(8)
				25	Cl1	C14	C15	119.4(7)
				26	C13	C14	C15	118.4(9)
				27	C14	C15	C16	120.1(9)
				28	C11	C16	C15	122.5(8)

Table 2. XRD-exp. torsion angles (°).

No.	Torsion				(°)
1	C8	S1	C7	C6	87.4(6)
2	C7	S1	C8	N1	-177.1(6)
3	C8	N1	N2	C9	-171.8(8)
4	N2	N1	C8	S1	-4.9(9)
5	N2	N1	C8	S2	175.8(6)
6	C6	C1	C2	C3	0(2)
7	C2	C1	C6	C5	-2(1)
8	C2	C1	C6	C7	-177.3(9)
9	N1	N2	C9	C10	-1(1)
10	N1	N2	C9	C11	178.4(7)
11	C1	C2	C3	C4	1(2)
12	C2	C3	C4	C5	-1(2)
13	C3	C4	C5	C6	-1(2)
14	C4	C5	C6	C1	2(1)
15	C4	C5	C6	C7	177.5(9)
16	C1	C6	C7	S1	-116.9(8)
17	C5	C6	C7	S1	68(1)
18	N2	C9	C11	C12	-167.2(8)
19	N2	C9	C11	C16	12(1)
20	C10	C9	C11	C12	12(1)
21	C10	C9	C11	C16	-168.5(8)
22	C9	C11	C12	C13	179.1(8)
23	C16	C11	C12	C13	-1(1)
24	C9	C11	C16	C15	179.5(8)
25	C12	C11	C16	C15	-1(1)
26	C11	C12	C13	C14	1(2)
27	C12	C13	C14	Cl1	179.7(8)
28	C12	C13	C14	C15	-1(2)
29	Cl1	C14	C15	C16	179.0(7)
30	C13	C14	C15	C16	-1(1)
31	C14	C15	C16	C11	2(1)

3.3. XRD-packing and HSA

Three types of interactions was reported in crystal lattice of the ligand, three 2D-supramolecular chain patterns of stable S(7) synthon C_{Me}-H….S=C with 2.772 Å and N-H…S=C H-bonds with 2.711Å (Fig.3a), the second S(14) synthon head-to-tail interactions via two C_{Ph}-H…S=C H-bond with 2.982 Å (Fig.3b). The third head-to-tail S(18) synthon C_{Me}-H….H-C_{Ph} with 2.260 Å were recorded (Fig.2c).

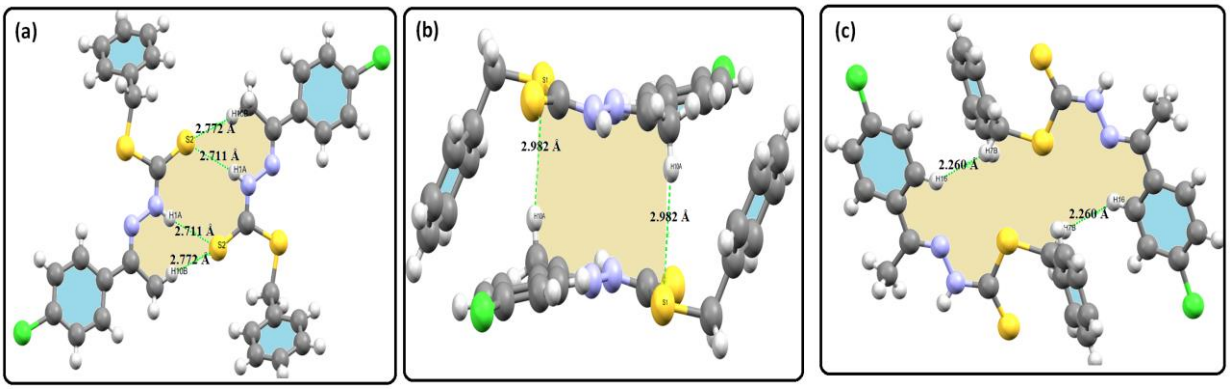


Fig. 3. The total interactions in the crystal lattice.

The HSA was carried out using CIF-file of crystal of the ligand [27-30]; the results are illustrated in Fig. 4, the 3D Hirshfeld mapped was represented in d_{norm}, shape index and curvedness, which were established in the range -0.443 to 1.323 a.u.. Eight red-holes were detected on the surface of ligand that is consistent with presence of several heteroatoms like S, N and Cl (Fig.4a). Several interactions due to NH….S and CH….S H-bonds interactions formations as reflected many big red-spots on the ligand surface. The shape index reflected the presence of polar proton electrophile indicated (blue) color and many nucleophilic (red) functional groups (Fig.4b). Moreover, the atom-to-atom fingerprint (FP) intermolecular percentage plot is illustrated in Fig.4e.

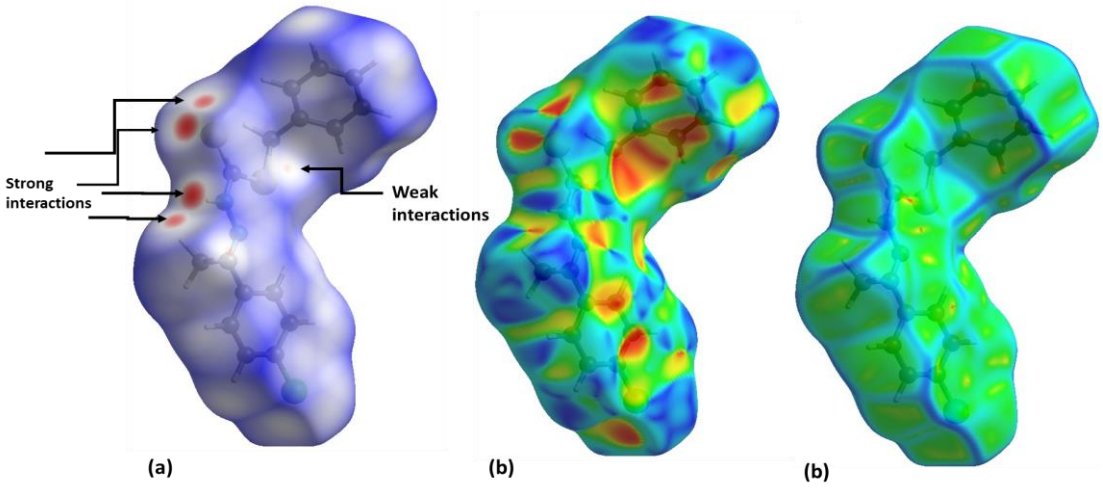


Fig.4. (a) d_{norm} and (b) shape index, and (c) curvedness HSA mapped over the ligand surface.

3.4. Two direction fingerprints (2D-FP)

The result showed the H⋯⋯H% as the highest contributors in both the compound atom-to-atom interactions with 60.1% meanwhile, the lowest contributors was found to be H….N 0.2%. The total 2D-FP H…Atoms ratios analyses for computed surface of the desired ligand found to be as H……H>C……H>S……H>Cl……H>N……H as seen in Fig.5.

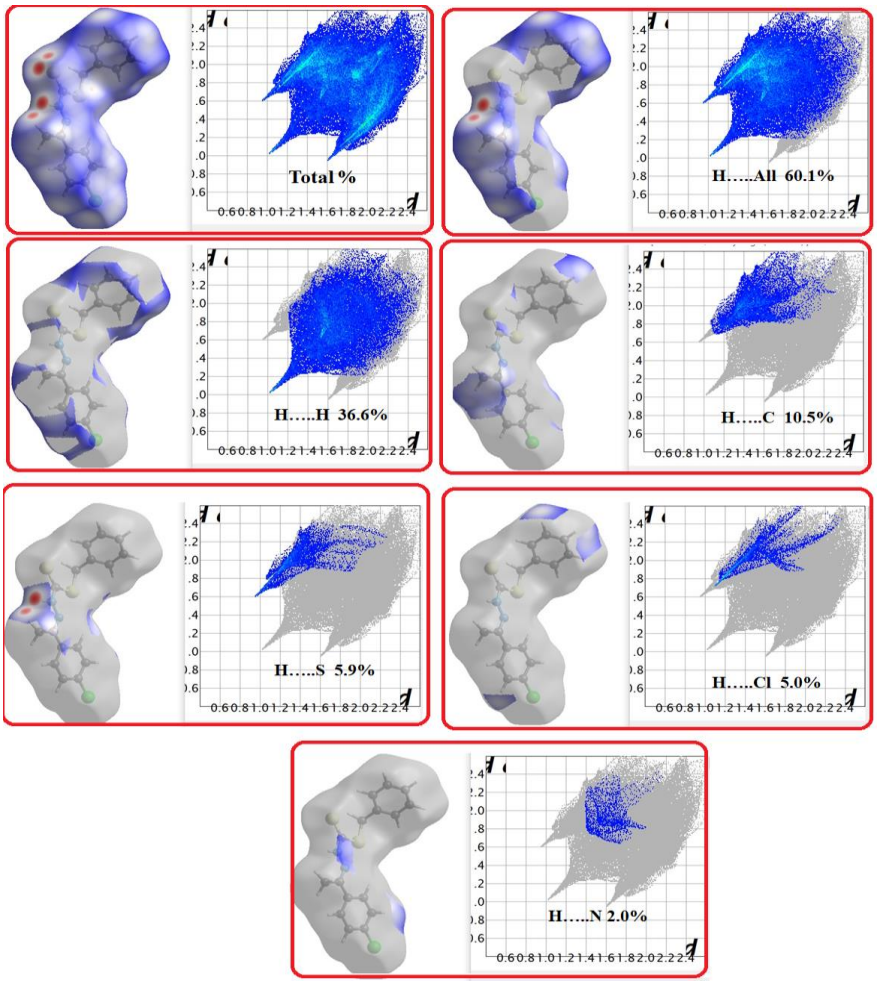


Fig.5. Inside/outside 2D-FP plots.

4. Conclusion

The dithiocarbazate S. B was synthesized in a high yield, centered was monitored by PXRD powder and XRD-crystal. The CHN-EA and MS analyses confirmed the expected ligand molecular formula. The thione isomer structure was proved by XRD-crystal; several polar interactions with two types of synthons were recorded. Moreover, the HSA and 2D-FT computations were successfully compared to the XRD-packing result to support the synthons formation via main NH….S and CH….S=C H-bonds interactions.

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Supplementary information:

Crystallographic data for the structural analysis has been deposited with the Cambridge crystallographic Data Centre, CCDC No. 2018704 for S-benzyl-β-N-(1-(4-chlorophenyl) ethylidene) dithiocarbazate a Copy of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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