Crystal structure and computational study of 2,4-dichloro-N-[(E)-(5-nitrothiophen-2-yl)methylidene]aniline

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The title compound, $C_{11}H_6Cl_2N_2O_2S$, is a Schiff base that incorporates an N-bound 2,4-dichlorophenyl and a C-bound 5-nitrothiophene ring. The molecule is approximately planar, the maximum deviation from the mean plane being 0.233 (4) Å for the C=N N atom. The dihedral angle between the benzene and thiophene rings is 9.7 (2)°. The C=N double bond has an E configuration. The crystal structure features C—H⋯O hydrogen bonds, forming sheets parallel to (10$\bar{1}$), and π–π stacking interactions between symmetry-related thiophene and benzene rings, in which the distance between adjacent ring centroids is 3.707 (4) Å, forming a three-dimensional supramolecular structure. Geometric parameters from quantum-chemical calculations are in good agreement with experimental X-ray diffraction results.

1. Chemical context

Schiff bases, which contain C=N double bonds, are well known starting materials for the synthesis of many drugs (Aydoğan et al., 2001) and often possess very important biological activities, such as anti-inflammatory and analgesic properties (Sondhi et al., 2006). In addition, nitrothiophene and its derivatives also exhibit many biological activities, including antibacterial and antifungal (Kalluraya et al., 1994; Kalluraya & Shetty, 1997) properties. We report the synthesis, structural analysis and theoretical calculations of the title compound, $C_{11}H_6Cl_2N_2O_2S$ (I), which is a new Schiff base that includes a nitrothiophene group.
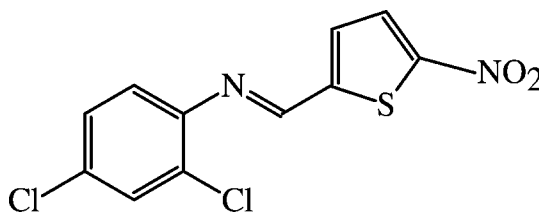
2. Structural commentary

The title compound (Fig. 1) is nearly planar, the maximum deviation from the mean plane of 0.233 (4) Å is for atom N2. Schiff bases that are derived from salicylaldehyde show thermochromism and photochromism properties that are dependent upon planarity or non-planarity of the molecules (Cohen et al., 1964; Hadjoudis et al., 1987). Since the dihedral angle
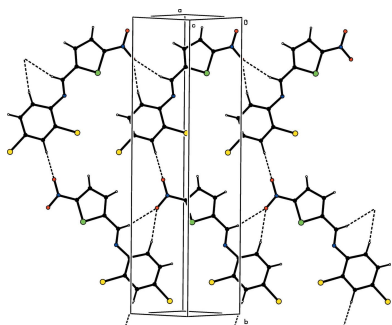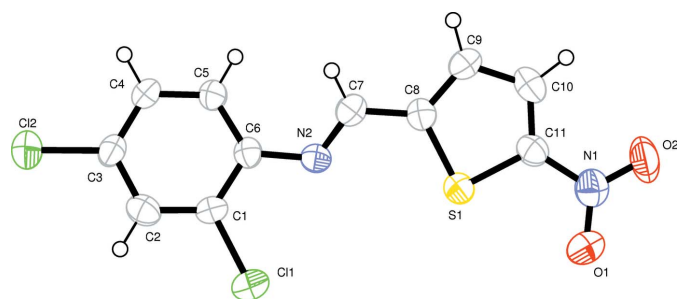
Figure 1
A view of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.

between the benzene and thiophene rings is 9.7 (2)°, the title compound may exhibit thermochromic features. The slight twist of the molecule is caused by a steric repulsion of atoms H5 and H7. The C7=N2 double-bond distance is 1.267 (6)Å, which is comparable to those of reported structures (Özdemir Tarı & Işık, 2012; Ceylan *et al.*, 2012). The C8—C7—N2—C6 torsion angle is 178.5 (5)°.

3. Supramolecular features

In the crystal structure there are weak C—H···O hydrogen bonds (Fig. 2 and Table 1) with atom O1 acting as a bifurcated acceptor from both C5 and C7 ($x - 1$, y, $z - 1$), creating an $R_2^1(7)$ motif, and forming sheets parallel to (10$\bar{1}$). π–π stacking interactions are present between the benzene (centroid $Cg2$) and thiophene (centroid $Cg1$) rings of symmetry-related molecules [$Cg1\cdots Cg2(x, \frac{3}{2} - y, \frac{1}{2} + z) = 3.707$ (4) Å, forming a three-dimensional supramolecular structure.
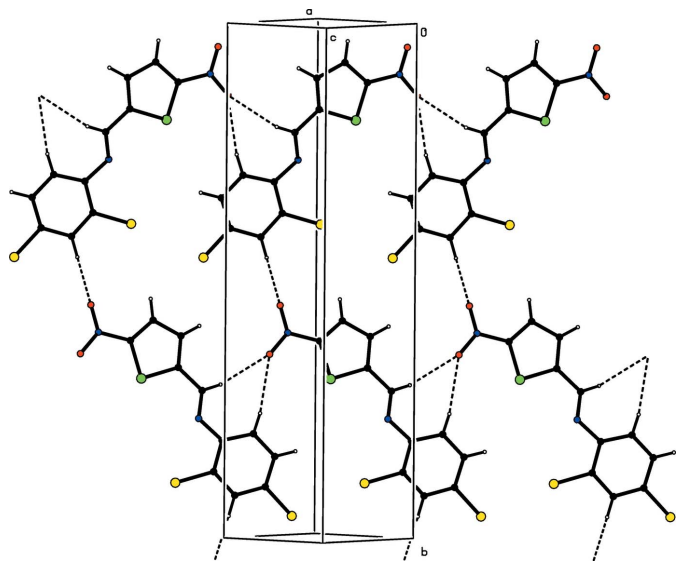

Figure 2
A partial packing view of (I). Dashed lines indicate the C—H···O hydrogen-bonding interactions

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O1^i	0.93	2.59	3.508 (8)	171
C7—H7···O1^i	0.93	2.55	3.300 (8)	138
C2—H2···O2^{ii}	0.93	2.56	3.360 (7)	144

Symmetry codes: (i) $x - 1, y, z - 1$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$.

4. Theoretical Calculations

Quantum-chemical calculations were performed to compare with the experimental analysis. *Ab initio* Hartree–Fock (HF) and density functional DFT(B3LYP) methods were used with the standard basis set of 6-31+G(d) (Becke, 1993; Lee *et al.*, 1988; Schlegel, 1982; Peng *et al.*, 1996) using the *Gaussian 03* software package (Frisch *et al.*, 2004; Dennington *et al.*, 2007) to obtain the optimized molecular structure. The computational results are consistent with experimental crystallographic data. The C7=N2 bond length was calculated to be 1.25 and 1.28 Å using HF and DFT(B3LYP) methods, respectively. The torsion angle C8—C7—N2—C6 was calculated to be −177.98 and −176.09° by HF and DFT(B3LYP) methods, respectively.

5. Synthesis and crystallization

The compound 2,4-dichloro-*N*-[(*E*)-(5-nitrothiophen-2-yl)methylidene]aniline was prepared by refluxing a mixture of a solution containing 5-nitro-2-thiophenecarboxaldehyde (0.0180 g, 0.114 mmol) in 20 ml ethanol and a solution containing 2,4-dichloroaniline (0.0185 g, 0.114 mmol) in 20 ml ethanol. The reaction mixture was stirred for 1h under reflux. Crystals suitable for X-ray analysis were obtained from a solution in ethanol by slow evaporation (yield 65%; m.p 443–445 K).

IR (KBr/cm^{-1}): 3102.59 (C—H), 1602.71 (C=N), 1503.00 (NO$_2$), 1231.00 (C—N, methylene), 1192.05 (C—N, thiophene), 1039.60 (C—H, thiophene), 1124.10 (C—H, methylene), 957.96 (C—H, methylene), 787.73 (C—H, 957.96)

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were positioned geometrically with C—H = 0.93 Å and refined with using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$.

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Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_6Cl_2N_2O_2S$
M_r	301.14
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	7.5731 (9), 22.1795 (16), 8.3093 (16)
β (°)	117.967 (10)
V (Å^3)	1232.7 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.69
Crystal size (mm)	$0.18 \times 0.15 \times 0.10$
Data collection	
Diffractometer	Agilent SuperNova (Single source at offset) Eos
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2011)
T_{min}, T_{max}	0.712, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3059, 2201, 1119
R_{int}	0.033
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.063, 0.138, 1.09
No. of reflections	2201
No. of parameters	163
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.38, −0.32

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2007), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012).

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supporting information

Crystal structure and computational study of 2,4-dichloro-*N*-[(*E*)-(5-nitrothiophen-2-yl)methylidene]aniline

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Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2007); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2007); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

2,4-Dichloro-*N*-[(*E*)-(5-nitrothiophen-2-yl)methylidene]aniline

Crystal data

$C_{11}H_6Cl_2N_2O_2S$	$F(000) = 608$
$M_r = 301.14$	$D_x = 1.623$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.5731 (9)$ Å	Cell parameters from 612 reflections
$b = 22.1795 (16)$ Å	$\theta = 3.2–28.4°$
$c = 8.3093 (16)$ Å	$\mu = 0.69$ mm^{-1}
$\beta = 117.967 (10)°$	$T = 293$ K
$V = 1232.7 (3)$ Å^3	Block, red
$Z = 4$	$0.18 \times 0.15 \times 0.10$ mm

Data collection

Agilent SuperNova (Single source at offset) Eos diffractometer	3059 measured reflections
Radiation source: SuperNova (Mo) X-ray Source	2201 independent reflections
	1119 reflections with $I > 2\sigma(I)$
Detector resolution: 16.0454 pixels mm^{-1}	$R_{int} = 0.033$
ω scans	$\theta_{max} = 26.0°$, $\theta_{min} = 3.2°$
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2011)	$h = -7 \rightarrow 9$
	$k = -27 \rightarrow 12$
$T_{min} = 0.712$, $T_{max} = 1.000$	$l = -10 \rightarrow 5$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.063$	H-atom parameters constrained
$wR(F^2) = 0.138$	$w = 1/[\sigma^2(F_o^2) + (0.019P)^2]$
$S = 1.09$	where $P = (F_o^2 + 2F_c^2)/3$
2201 reflections	$(\Delta/\sigma)_{max} < 0.001$
163 parameters	$\Delta\rho_{max} = 0.38$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.32$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.4933 (2)	0.69183 (7)	0.38617 (19)	0.0450 (4)
Cl1	0.3105 (3)	0.89412 (7)	0.2025 (2)	0.0612 (5)
Cl2	−0.2711 (3)	0.95859 (7)	−0.4521 (2)	0.0720 (6)
C6	0.0675 (8)	0.8117 (2)	−0.0461 (7)	0.0369 (14)
C7	0.1939 (9)	0.7153 (3)	0.0411 (7)	0.0473 (16)
H7	0.1199	0.7042	−0.0806	0.057*
C5	−0.0926 (8)	0.7988 (3)	−0.2169 (7)	0.0443 (15)
H5	−0.1307	0.7588	−0.2472	0.053*
C2	0.0113 (9)	0.9185 (3)	−0.1289 (7)	0.0468 (16)
H2	0.0445	0.9588	−0.0990	0.056*
C4	−0.1955 (9)	0.8429 (3)	−0.3414 (7)	0.0446 (15)
H4	−0.3005	0.8328	−0.4545	0.053*
O1	0.8046 (7)	0.6438 (2)	0.7224 (6)	0.0768 (15)
N2	0.1847 (7)	0.7692 (2)	0.0870 (6)	0.0429 (12)
C10	0.4560 (10)	0.5791 (3)	0.3021 (8)	0.0499 (16)
H10	0.4750	0.5376	0.3102	0.060*
N1	0.7237 (8)	0.6023 (2)	0.6127 (7)	0.0538 (14)
C1	0.1141 (8)	0.8726 (2)	−0.0056 (7)	0.0395 (14)
O2	0.7734 (7)	0.5493 (2)	0.6444 (6)	0.0761 (15)
C9	0.3146 (9)	0.6094 (3)	0.1475 (7)	0.0495 (17)
H9	0.2288	0.5902	0.0393	0.059*
C11	0.5608 (9)	0.6182 (3)	0.4372 (8)	0.0450 (15)
C8	0.3165 (9)	0.6706 (3)	0.1730 (7)	0.0445 (15)
C3	−0.1422 (9)	0.9020 (3)	−0.2976 (7)	0.0436 (15)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0440 (10)	0.0394 (9)	0.0480 (9)	0.0004 (8)	0.0184 (8)	0.0007 (7)
Cl1	0.0617 (12)	0.0609 (11)	0.0451 (9)	−0.0060 (9)	0.0118 (9)	−0.0096 (8)
Cl2	0.0749 (15)	0.0527 (10)	0.0616 (11)	0.0061 (10)	0.0096 (11)	0.0135 (9)
C6	0.041 (4)	0.038 (3)	0.036 (3)	0.004 (3)	0.022 (3)	0.004 (3)
C7	0.051 (4)	0.050 (4)	0.037 (3)	0.000 (3)	0.017 (3)	0.002 (3)
C5	0.037 (4)	0.039 (3)	0.046 (3)	0.003 (3)	0.009 (3)	0.002 (3)
C2	0.051 (4)	0.042 (4)	0.053 (4)	−0.009 (3)	0.029 (4)	−0.003 (3)
C4	0.041 (4)	0.047 (4)	0.033 (3)	0.001 (3)	0.007 (3)	0.001 (3)
O1	0.069 (4)	0.067 (3)	0.060 (3)	−0.008 (3)	0.001 (3)	−0.003 (3)
N2	0.042 (3)	0.037 (3)	0.045 (3)	−0.005 (2)	0.016 (3)	−0.001 (2)
C10	0.064 (5)	0.036 (3)	0.060 (4)	0.006 (3)	0.038 (4)	0.003 (3)

N1	0.049 (4)	0.055 (4)	0.061 (4)	0.004 (3)	0.029 (3)	0.007 (3)
C1	0.037 (4)	0.044 (4)	0.036 (3)	−0.006 (3)	0.016 (3)	−0.004 (3)
O2	0.086 (4)	0.053 (3)	0.082 (3)	0.028 (3)	0.033 (3)	0.021 (2)
C9	0.052 (5)	0.053 (4)	0.036 (3)	−0.001 (3)	0.014 (3)	−0.001 (3)
C11	0.049 (4)	0.039 (3)	0.049 (4)	−0.004 (3)	0.025 (4)	0.002 (3)
C8	0.042 (4)	0.042 (3)	0.046 (4)	0.003 (3)	0.018 (3)	0.003 (3)
C3	0.041 (4)	0.049 (4)	0.033 (3)	0.003 (3)	0.011 (3)	0.005 (3)

Geometric parameters (Å, º)

S1—C11	1.703 (6)	C2—C1	1.394 (7)
S1—C8	1.711 (6)	C2—H2	0.9300
Cl1—C1	1.737 (5)	C4—C3	1.370 (7)
Cl2—C3	1.732 (6)	C4—H4	0.9300
C6—C5	1.397 (7)	O1—N1	1.237 (6)
C6—C1	1.398 (7)	C10—C11	1.344 (7)
C6—N2	1.407 (6)	C10—C9	1.399 (7)
C7—N2	1.267 (6)	C10—H10	0.9300
C7—C8	1.446 (7)	N1—O2	1.226 (6)
C7—H7	0.9300	N1—C11	1.445 (7)
C5—C4	1.371 (7)	C9—C8	1.372 (7)
C5—H5	0.9300	C9—H9	0.9300
C2—C3	1.386 (7)		
C11—S1—C8	89.5 (3)	C9—C10—H10	124.6
C5—C6—C1	116.3 (5)	O2—N1—O1	124.1 (6)
C5—C6—N2	126.1 (5)	O2—N1—C11	118.8 (5)
C1—C6—N2	117.6 (5)	O1—N1—C11	117.1 (5)
N2—C7—C8	121.7 (5)	C2—C1—C6	122.5 (5)
N2—C7—H7	119.2	C2—C1—Cl1	117.0 (4)
C8—C7—H7	119.2	C6—C1—Cl1	120.4 (4)
C4—C5—C6	122.5 (6)	C8—C9—C10	112.6 (5)
C4—C5—H5	118.8	C8—C9—H9	123.7
C6—C5—H5	118.8	C10—C9—H9	123.7
C3—C2—C1	117.8 (5)	C10—C11—N1	125.2 (6)
C3—C2—H2	121.1	C10—C11—S1	114.8 (5)
C1—C2—H2	121.1	N1—C11—S1	120.0 (4)
C3—C4—C5	119.3 (5)	C9—C8—C7	127.2 (6)
C3—C4—H4	120.3	C9—C8—S1	112.2 (4)
C5—C4—H4	120.3	C7—C8—S1	120.6 (5)
C7—N2—C6	119.9 (5)	C4—C3—C2	121.6 (5)
C11—C10—C9	110.8 (6)	C4—C3—Cl2	120.2 (4)
C11—C10—H10	124.6	C2—C3—Cl2	118.2 (5)
C1—C6—C5—C4	2.0 (8)	O1—N1—C11—C10	−179.9 (6)
N2—C6—C5—C4	−177.9 (5)	O2—N1—C11—S1	−177.9 (5)
C6—C5—C4—C3	−0.7 (9)	O1—N1—C11—S1	2.2 (7)
C8—C7—N2—C6	178.5 (5)	C8—S1—C11—C10	−0.3 (5)

C5—C6—N2—C7	22.1 (9)	C8—S1—C11—N1	177.9 (5)
C1—C6—N2—C7	−157.7 (5)	C10—C9—C8—C7	178.5 (5)
C3—C2—C1—C6	−0.2 (8)	C10—C9—C8—S1	0.6 (7)
C3—C2—C1—Cl1	178.2 (4)	N2—C7—C8—C9	168.4 (6)
C5—C6—C1—C2	−1.5 (8)	N2—C7—C8—S1	−13.8 (8)
N2—C6—C1—C2	178.4 (5)	C11—S1—C8—C9	−0.2 (5)
C5—C6—C1—Cl1	−179.9 (3)	C11—S1—C8—C7	−178.3 (5)
N2—C6—C1—Cl1	0.0 (7)	C5—C4—C3—C2	−1.2 (9)
C11—C10—C9—C8	−0.8 (8)	C5—C4—C3—Cl2	−179.6 (4)
C9—C10—C11—N1	−177.4 (5)	C1—C2—C3—C4	1.6 (8)
C9—C10—C11—S1	0.6 (7)	C1—C2—C3—Cl2	−180.0 (4)
O2—N1—C11—C10	0.0 (9)		

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C5—H5⋯O1[i]	0.93	2.59	3.508 (8)	171
C7—H7⋯O1[i]	0.93	2.55	3.300 (8)	138
C2—H2⋯O2[ii]	0.93	2.56	3.360 (7)	144

Symmetry codes: (i) $x-1, y, z-1$; (ii) $-x+1, y+1/2, -z+1/2$.