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(*E*)-*N*-[(Benzo[*b*]thiophen-3-yl)methylene]-*N*′-(2,5-dichlorophenyl)-hydrazine

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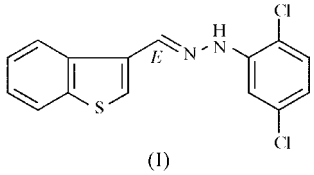
The title compound, $C_{15}H_{10}Cl_2N_2S$, crystallizes in the centrosymmetric space group $P2_1/c$ with one molecule in the asymmetric unit. The molecule assumes an approximately planar configuration and has an *E* geometry about the azomethine C=N double bond. The crystal structure is stabilized by extensive hydrogen bonding.

Comment

Tuberculosis is a contagious disease caused by *Mycobacterium tuberculosis*. After a long period during which this disease seemed to be declining, the last two decades have seen an unexpected return recorded (Raviglione *et al.*, 1995). Isoniazid, pyraziniamide, ethambutol, rifampicin and streptomycin, generally used in combination, are still the current drugs of choice in the therapy of tuberculosis (Lounis *et al.*, 1997). Numerous recent reports in the literature provide evidence of renewed interest as the search for new antitubercular agents continues. A series of novel hydrazones were synthesized and screened for antitubercular activity at the Tuberculosis Antimicrobial Acquisition and Coordinating Facility (TAACF), and the title compound, (I), was found to be very active, with 96% inhibition in the preliminary screen at 6.25 μg ml^{-1}.



(I)

Compound (I) was prepared by condensation of benzo[*b*]-thiophene-3-carboxaldehyde with 2,5-dichlorophenylhydrazine to afford a single geometrical isomer. The structure of the product, (I), was initially identified by NMR spectroscopy. In order to confirm the double-bond geometry of this compound, and to obtain more detailed information on the structural conformation of the molecule which may be of value in structure–activity analysis, the X-ray structure determination of (I) has been carried out and the results are presented here.

The molecules of (I) adopt an *E* geometry about the azomethine C=N double bond, with atom C2 of the benzo[*b*]thiophene moiety and the 2,5-dichlorophenyl group on opposite sides of the C9=N10 bond. Overall, the molecule is planar, with an N11—N10—C9—C2 torsion angle of 179.3 (2)° (Fig. 1). The r.m.s. deviation of the non-H atoms from the least-squares mean plane is only 0.018 (13) Å. This configuration is in agreement with common observations in phenylhydrazone derivatives. The N10—N11 bond distance of 1.371 (3) Å is shorter than a normal N—N single bond, as in the case of 2,4-dinitrophenylhydrazine [1.405 (6) Å; Okabe *et al.*, 1993], which suggests delocalization of the azomethine double bond in the benzo[*b*]thiophene system, and this observation is further supported by the shortened C2—C9 bond length [1.450 (4) Å] compared with the standard value

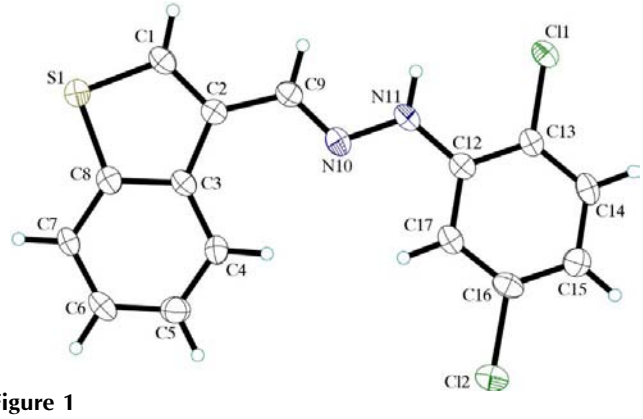


Figure 1
A view of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

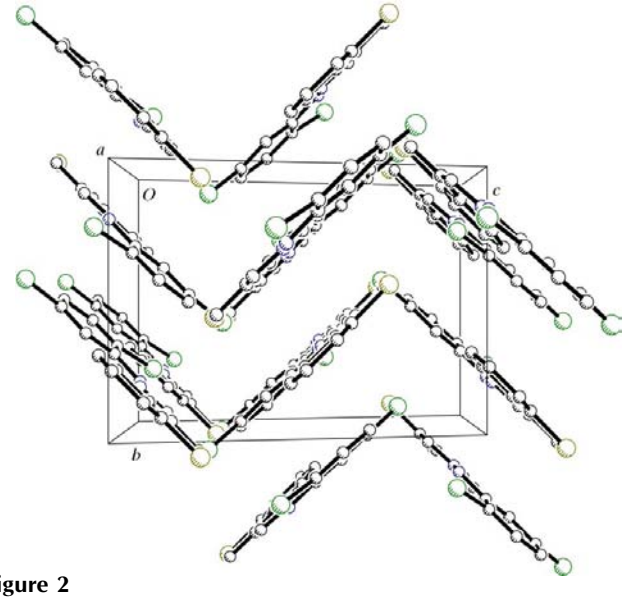


Figure 2
The crystal packing of (I), viewed along the *a* axis. H atoms have been omitted for clarity.

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for a $C_{ar}-Csp^2$ single bond (ar is aryl; Wilson, 1992). Also, the N11—C12 bond distance of 1.387 (4) Å (Table 1) indicates partial double-bond character between atom N11 and atom C12 of the 2,5-dichlorophenyl ring.

Intermolecular hydrogen bonding exists between the imino H atom and the Cl atoms (Table 2) and gives rise to chains of molecules extending in the *c* direction. The mode of packing of (I) along the *a* direction is illustrated in Fig. 2 and van der Waals forces contribute to the stabilization of the crystal structure.

Experimental

A mixture of 2,5-dichlorophenylhydrazine (0.531 g, 3 mmol) and benzo[*b*]thiophene-3-carboxaldehyde (0.487 g, 3 mmol) was dissolved in methanol (10 ml) and the solution was refluxed for 2 h. After cooling the reaction mixture, crystals of (I) formed and were collected by filtration. Recrystallization of the product from methanol afforded pale-yellow plates suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$, δ): 6.78 (*dd*, *J* = 7.8 and 2.4 Hz, 1H), 7.42 (*d*, *J* = 8.7 Hz, 1H), 7.44 (*t*, *J* = 7.5 Hz, 1H), 7.55 (*t*, *J* = 7.5 Hz, 1H), 7.59 (*d*, *J* = 2.4 Hz, 1H), 7.61 (*s*, 1H), 7.88 (*d*, *J* = 8.4 Hz, 1H), 8.00 (*s*, 1H), 8.69 (*d*, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, δ): 114.0, 115.2, 119.9, 122.8, 124.9, 125.3, 125.4, 128.8, 130.1, 131.4, 134.1, 136.0, 137.1, 140.8, 141.4.

Crystal data

$C_{15}H_{10}Cl_2N_2S$
M_r = 321.21
Monoclinic, $P2_1/c$
a = 13.2826 (5) Å
b = 8.7162 (3) Å
c = 12.7914 (4) Å
β = 111.4827 (17)°
V = 1378.03 (8) Å^3
Z = 4
D_x = 1.548 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3368 reflections
θ = 1.0–27.5°
μ = 0.61 mm^{-1}
T = 90.0 (2) K
Plate, pale yellow
0.22 × 0.20 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans at fixed χ = 55°
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.877, T_{max} = 0.970
6100 measured reflections
3162 independent reflections
1987 reflections with $I > 2\sigma(I)$
R_{int} = 0.058
θ_{max} = 27.5°
h = −17 → 17
k = −11 → 11
l = −16 → 16

Table 1
Selected geometric parameters (Å, °).

Cl1—C13	1.735 (3)	C2—C9	1.450 (4)
S1—C1	1.719 (3)	C9—N10	1.283 (3)
S1—C8	1.740 (3)	N10—N11	1.371 (3)
C1—C2	1.363 (4)	N11—C12	1.387 (4)
C1—S1—C8	91.07 (14)	C9—N10—N11	116.2 (2)
C9—C2—C3	126.7 (3)	N10—N11—C12	119.4 (2)
N10—C9—C2	122.3 (3)	N11—C12—C17	121.4 (3)
S1—C1—C2—C9	179.5 (2)	N10—N11—C12—C17	−5.9 (4)
C1—C2—C9—N10	176.8 (3)	N10—N11—C12—C13	173.5 (2)
C3—C2—C9—N10	−3.6 (4)	N11—C12—C13—C14	178.6 (2)
C9—N10—N11—C12	−176.5 (2)	N11—C12—C13—Cl1	−2.7 (4)

Table 2
Hydrogen-bonding and short-contact geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···N10	0.95	2.49	3.059 (3)	118
C17—H17···N10	0.95	2.49	2.789 (4)	98
N11—H11···Cl1	0.88	2.56	2.960 (2)	109
N11—H11···Cl2^{i}	0.88	2.78	3.637 (3)	166
C17—H17···Cl2^{ii}	0.95	2.95	3.457 (3)	115

Symmetry codes: (i) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.121
S = 1.42
3162 reflections
181 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0598P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL*/*PC* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL*97 and local procedures.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1668). Services for accessing these data are described at the back of the journal.

References

Lounis, N., Ji, B., Truffot-Pernot, C. & Grosset, J. (1997). *Antimicrob. Agents Chemother.* **41**, 607–610.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Okabe, N., Nakamura, T. & Fukuda, H. (1993). *Acta Cryst.* C**49**, 1678–1680.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Raviglione, M. C., Snider, D. E. & Kochi, A. (1995). *J. Am. Med. Assoc.* **273**, 220–226.
Sheldrick (1995). *XP* in *SHELXTL*/*PC*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Wilson, A. J. C. (1992). Editor. *International Tables for Crystallography*, Vol. C, Table 9.5.1.1. Dordrecht: Kluwer Academic Publishers.