Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

N-(2,5-Dichlorophenyl)-*N*′-[(*E*)-3-thienylmethylene]hydrazine

Vijayakumar N. Sonar,[a] Sean Parkin[b] and Peter A. Crooks[a]*

[a]Department of Pharmaceutical Sciences, College of Pharmacy, University of Kentucky, Lexington, KY 40536, USA, and [b]Department of Chemistry, University of Kentucky, Lexington, KY 40506, USA

Correspondence e-mail: pcrooks@uky.edu

Key indicators

Single-crystal X-ray study
T = 90 K
Mean σ(C–C) = 0.003 Å
R factor = 0.038
wR factor = 0.109
Data-to-parameter ratio = 18.2

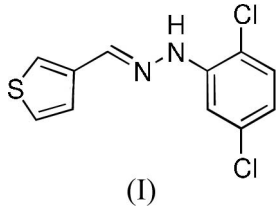
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 20 May 2005
Accepted 22 May 2005
Online 28 May 2005

The title compound, $C_{11}H_8Cl_2N_2S$, was prepared from the condensation reaction of thiophene-3-carbaldehyde with 2,5-dichlorophenylhydrazine. The azomethine C=N bond has *E* geometry. No thienyl ring flip was observed.

Comment

After a long period during which tuberculosis seemed to be declining, the last two decades have seen an unexpected return (Raviglione *et al.*, 1995). Numerous recent reports in the literature provide evidence of renewed interest as the search for new antitubercular agents continues. A series of novel hydrazones have been synthesized and screened for antitubercular activity at the Tuberculosis Antimicrobial Acquisition and Coordinating Facility (TAACF), and the title compound, (I), showed 70% growth inhibition in the preliminary screen against *Mycobacterium tuberculosis* at 6.25 μg ml^{-1}. The title compound was prepared from the condensation reaction of thiophene-3-carboxaldehyde with 2,5-dichlorophenylhydrazine, which afforded a single geometrical isomer. In order to confirm the C=N double-bond geometry of this compound, and to obtain more detailed information on the structural conformation of the molecule, its X-ray structure determination has been carried out and the results are presented here.



(I)

The molecular structure and atom-numbering scheme of (I) are shown in Fig. 1, and selected bond lengths and angles are listed in Table 1. In the molecule of (I), the C=N bond connecting the 2,5-dichlorophenylamino and thiophene rings has *E* geometry, with the two rings on opposite sides of the C7=N2 bond. The molecule is nearly planar, with an N1—N2=C7—C8 torsion angle of 178.71 (18)° (Fig. 1). The N1—N2 bond distance of 1.368 (2) 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], suggesting delocalization of the azomethine double bond with the thiophene ring. This observation is further supported by the shortening of the C7—C8 bond [1.445 (3) Å] compared with the standard value for a C_{ar}—Csp^2 single bond (Allen *et al.*, 1992). Also, the N1—C1 bond distance of 1.383 (3) Å (Table 1) indicates partial

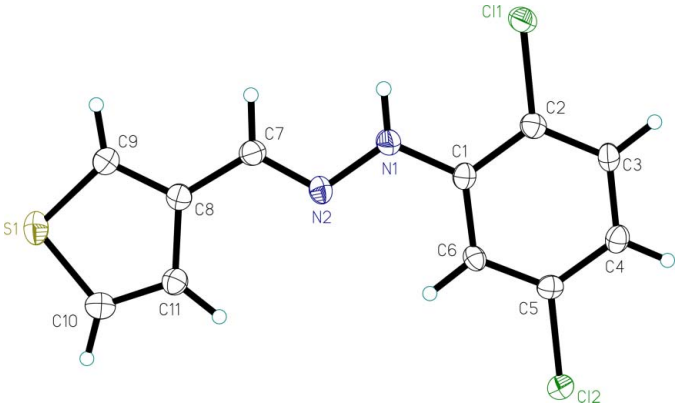


Figure 1
A view of the molecule (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

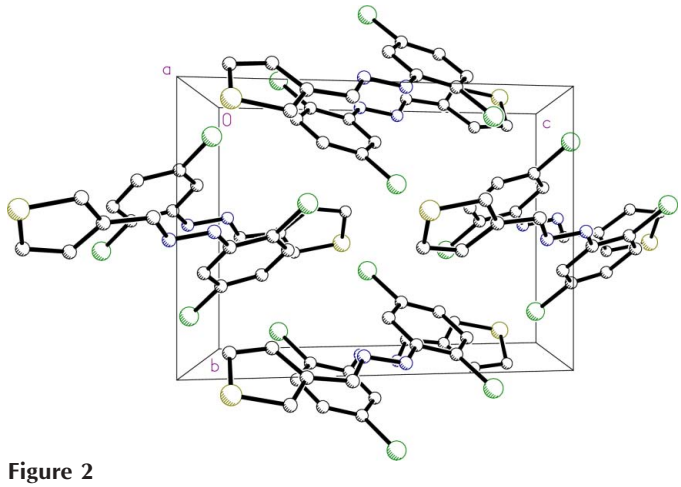


Figure 2
A packing diagram for (I), viewed down the *a* axis. H atoms have been omitted.

double-bond character between atom N1 and atom C1 of the 2,5-dichlorophenyl ring.

The mode of packing of (I) along the *a* direction is illustrated in Fig. 2. Intermolecular hydrogen bonding exists between the imino H and the Cl atoms (Table 2), and this contributes to the stabilization of the crystal structure.

Experimental

A mixture of thiophene-3-carboxaldehyde (0.336 g, 3 mmol) and 2,5-dichlorophenylhydrazine (0.531 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. Crystallization from methanol gave (I) as a brown blocks which were suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$, δ, p.p.m.): 6.75 (*dd*, 1H), 7.17 (*d*, 1H), 7.35 (*q*, 1H), 7.43 (*dd*, 1H), 7.55 (*m*, 2H), 7.89 (*s*, 2H); ^{13}C NMR ($CDCl_3$, δ, p.p.m.): 114.1, 115.1, 119.8, 124.9, 125.2, 126.7, 130.0, 134.0, 136.3, 137.7, 141.4.

Crystal data

$C_{11}H_8Cl_2N_2S$
M_r = 271.15
Monoclinic, $P2_1/c$
a = 12.3563 (2) Å
b = 8.3200 (2) Å
c = 11.6818 (3) Å
β = 106.2747 (10)°
V = 1152.82 (5) Å^3
Z = 4
D_x = 1.562 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2826 reflections
θ = 1.0–27.5°
μ = 0.71 mm^{-1}
T = 90.0 (2) K
Block, brown
0.20 × 0.20 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.870, T_{max} = 0.900
5066 measured reflections
2640 independent reflections
2054 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 27.5°
$h = -16 \rightarrow 15$
$k = -10 \rightarrow 10$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.109
S = 1.09
2640 reflections
145 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + 0.1691P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—N2	1.368 (2)	S1—C9	1.705 (2)
N1—C1	1.383 (3)	S1—C10	1.709 (2)
N2—C7	1.283 (3)	C7—C8	1.445 (3)
N2—N1—C1	119.83 (17)	N1—C1—C2	119.38 (18)
C7—N2—N1	116.31 (18)	N2—C7—C8	120.8 (2)
C9—S1—C10	92.38 (11)	C9—C8—C7	123.8 (2)
C1—N1—N2—C7	−168.53 (19)	N1—N2—C7—C8	178.71 (18)
N2—N1—C1—C6	−5.6 (3)	N2—C7—C8—C9	−178.1 (2)
N2—N1—C1—C2	175.71 (18)	N2—C7—C8—C11	−1.8 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1	0.88	2.52	2.9395 (17)	110

H atoms were positioned geometrically and treated as riding, with N—H = 0.88 Å and C—H = 0.95 Å, and with U_{iso}(H) = 1.2U_{eq}(C,N).

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97* and local procedures.

This investigation was supported by the National Institute of Alcohol Abuse and Alcoholism, grant No. AA12600. The measurement of the *in vitro* antitubercular activity was carried

out by the Tuberculosis Antimicrobial Acquisition and Coordinating Facility (TAACF) at the National Institute of Allergy and Infectious Disease, Southern Research Institute, GWL Hansens Disease Center and Colorado State University, USA.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1992). *International Tables for Crystallography*, Vol. C, edited by A. J. C. Wilson, pp. 685–706. Dordrecht: Kluwer Academic Publishers.

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). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.