

H atoms refined with $U = 1.2U_{eq}$ of the connected atom, with a length restraint of $1.00 \pm 0.05 \text{ \AA}$.

Scattering factors from *International Tables for Crystallography* (Vol. C)

Acta Cryst. (1998). C54, 527–529

Thiophene-2-carbaldehyde *N*-(2,4-Dinitrophenyl)-*N*-methylhydrazone

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(Received 1 April 1997; accepted 10 November 1997)

Table 1. Selected geometric parameters (Å, °)

C5—C6	1.392 (2)	C16—O19	1.362 (2)
C6—C7	1.468 (2)	C17—O18	1.348 (2)
C7—O11	1.241 (2)	O19—C20	1.423 (2)
C7—C8	1.423 (3)	S21—O24	1.432 (2)
C8—C9	1.360 (2)	S21—O23	1.450 (2)
C9—O10	1.370 (2)	S21—O22	1.472 (1)
C14—S21	1.770 (2)		
O11—C7—C8	123.6 (2)	O23—S21—O22	109.8 (1)
O11—C7—C6	119.3 (2)	O24—S21—C14	107.6 (1)
C5—O10—C9	121.12 (12)	O23—S21—C14	107.2 (1)
O24—S21—O23	114.5 (1)	O22—S21—C14	105.7 (1)
O24—S21—O22	111.6 (1)		
C8—C9—C12—C13	174.8 (2)	C15—C14—S21—O24	16.6 (2)
O10—C9—C12—C13	-6.0 (2)	C13—C14—S21—O23	72.2 (2)
C8—C9—C12—C17	-5.1 (3)	C15—C14—S21—O23	-107.1 (2)
O10—C9—C12—C17	174.2 (2)	C13—C14—S21—O22	-44.9 (2)
C17—C16—O19—C20	176.0 (2)	C15—C14—S21—O22	135.9 (1)
C13—C14—S21—O24	-164.2 (2)		

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

D—H...A	D—H	H...A	D...A	D—H...A
O18—H18...O11 ⁱ	0.92 (2)	1.79 (2)	2.658 (3)	155 (3)
N31—H311...O22 ⁱⁱ	1.01 (2)	1.82 (2)	2.820 (3)	174 (3)
N31—H312...O22	1.03 (2)	1.81 (2)	2.823 (3)	169 (3)
N31—H313...O33	0.95 (2)	1.80 (2)	2.726 (3)	166 (3)
O33—H331...O23 ⁱⁱⁱ	0.92 (2)	1.91 (2)	2.812 (3)	165 (3)
O33—H332...O24 ^{iv}	0.97 (2)	1.80 (2)	2.762 (3)	176 (3)

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

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD-4 Operations Manual*. Data reduction: *DATARED* (Pèpe, 1979). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1030). Services for accessing these data are described at the back of the journal.

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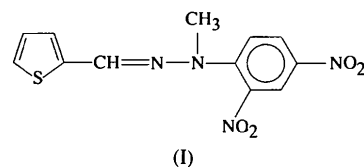
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Abstract

Molecules of the title compound, $C_{12}H_{10}N_4O_4S$, are linked through intermolecular hydrogen bonds to form a dimeric structure. The crystal structure of the dimer is stabilized by two intermolecular hydrogen bonds of the C—H...O type. The C...O intermolecular contact distance is 3.339 (3) Å, and the C=N and N—N distances are 1.279 (2) and 1.371 (7) Å, respectively. One O atom of the 2-nitro group is disordered over two sites.

Comment

As a result of their anti-HIV and anticancer activities, the chemical and pharmacological properties of arylhydrazones have been studied extensively (Öcal & Kaban, 1998). In this paper, we report the structure of thiophene-2-carbaldehyde *N*-(2,4-dinitrophenyl)-*N*-methylhydrazone, (I).



An *ORTEPII* (Johnson, 1976) plot of the title molecule is shown in Fig. 1. The bond lengths and angles in the thiophene and dinitrophenyl rings are in agreement with related structures reported previously (Rodino-Pinera *et al.*, 1996; Lu *et al.*, 1996). The hydrazone moiety (C7—N3—N4—C8) is almost in the plane of the thiophene ring. The dihedral angle between the dinitrophenyl and thiophene rings is 23.79 (11)°, and these two planes form angles of 25.43 (10) and 2.86 (10)°, respectively, with the plane of the central hydrazone moiety. The 2-nitro group is tilted 49.8 (2)° from the plane of the phenyl ring, whereas the 4-nitro group is almost coplanar with the ring. However, of the two disordered components of O1, the first (O1A)

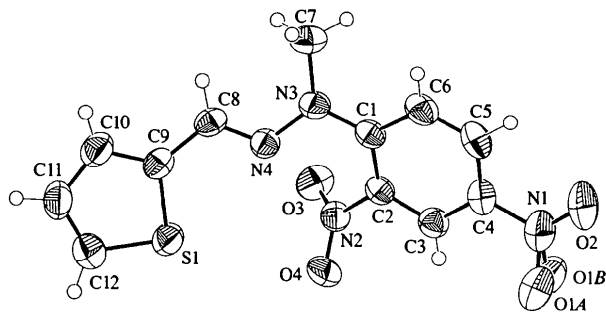


Fig. 1. ORTEPII (Johnson, 1976) view of the title molecule with the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary size.

deviates 0.48 (4) Å above and the second (O1B) deviates 0.12 (5) Å below the plane. The site-occupation factor of the major component refined to 0.57 (8). The C8=N4 bond length of 1.279 (2) Å is typical of a double bond.

The intermolecular C—H···O hydrogen-bonding network consists of dimer units. The structure is centrosymmetric, with the halves of the dimer related by a crystallographic inversion centre located in the centre of the 22-membered ring. The geometry of the hydrogen bond is C12···O4ⁱ 3.339 (3) Å, C12—H12 0.94 (2) Å and C12—H12···O4ⁱ 145.9 (17)° [symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$]. The resulting hydrogen-bonding geometry has been reported (Poméj-Hernández *et al.*, 1996). Bond angles around C9 suggest that there is an interaction between S1 and N4. The C10—C9—C8 and S1—C9—C8 bond angles are 127.5 (2) and 122.0 (2)°, respectively. The S···N distance is 3.002 (2) Å, which is shorter than the sum of the van der Waals radii (3.35 Å; Bondi, 1964).

Experimental

The title compound was synthesized by adding a solution of thiophene-2-carbaldehyde (1.34 mmol) in 10 ml absolute ethanol to a hot ethanolic solution of *N*-(2,4-dinitrophenyl)-*N*-methylhydrazine (1.34 mmol) and refluxing the reaction mixture for 2–3 h. On cooling, the separated solid was filtered and recrystallized from acetone–ethanol (1:1) to yield the title hydrazone for X-ray diffraction measurements.

Crystal data

C₁₂H₁₀N₄O₄S
M_r = 306.30
 Monoclinic
*C*2/*c*
a = 17.108 (2) Å
b = 10.450 (2) Å
c = 15.188 (3) Å
 β = 93.33 (5)°
V = 2710.7 (8) Å³
Z = 8
D_x = 1.501 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71070 Å
 Cell parameters from 25 reflections
 θ = 11.64–20.93°
 μ = 0.26 mm⁻¹
T = 293 (2) K
 Prismatic
 0.4 × 0.2 × 0.2 mm
 Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scans (North *et al.*, 1968)
 T_{\min} = 0.943, T_{\max} = 0.949
 2564 measured reflections
 2462 independent reflections

2075 reflections with $I > 2\sigma(I)$
 R_{int} = 0.009
 θ_{max} = 26.58°
 h = -21 → 21
 k = -13 → 0
 l = -19 → 0
 3 standard reflections
 frequency: 120 min
 intensity decay: 0.628%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.035
 $wR(F^2)$ = 0.077
 S = 0.973
 2462 reflections
 241 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0238P)^2 + 2.7183P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}}$ = 0.005
 $\Delta\rho_{\text{max}}$ = 0.23 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.18 e Å⁻³
 Extinction correction: SHELXL93
 Extinction coefficient: 0.00065 (11)
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

S1—C12	1.709 (2)	N3—N4	1.371 (2)
S1—C9	1.722 (2)	N3—C1	1.375 (2)
O1A—N1	1.27 (2)	N3—C7	1.455 (2)
O1B—N1	1.207 (13)	N4—C8	1.279 (2)
O2—N1	1.222 (2)	C8—C9	1.441 (3)
O3—N2	1.218 (2)	C9—C10	1.364 (3)
O4—N2	1.220 (2)	C10—C11	1.406 (3)
N1—C4	1.453 (3)	C11—C12	1.334 (3)
N2—C2	1.471 (2)		
C12—S1—C9	91.63 (11)	N4—N3—C7	122.2 (2)
O1B—N1—O2	121.2 (7)	C8—N4—N3	120.24 (15)
O2—N1—O1A	123.6 (8)	N4—C8—C9	119.3 (2)
O3—N2—O4	124.3 (2)	C10—C9—S1	110.4 (2)
N4—N3—C1	114.69 (14)	C11—C12—S1	111.9 (2)
C1—N3—N4—C8	175.5 (2)	N3—N4—C8—C9	179.6 (2)
N4—N3—C1—C2	24.8 (2)	N4—C8—C9—S1	-4.2 (3)
C2—C3—C4—N1	-179.3 (2)	C10—C11—C12—S1	0.0 (3)

Data were corrected for Lorentz, polarization and absorption effects. The structure was solved by direct methods and refined by full-matrix least-squares techniques. The H atoms were located from difference maps and refined isotropically. The C—H bond distances range from 0.88 (2) to 0.99 (2) Å, while U_{iso} values for H atoms are in the range 0.045 (5)–0.082 (8) Å².

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994). Cell refinement: CAD-4 EXPRESS. Data reduction: MolEN (Fair, 1990). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

The authors wish to acknowledge for the use of the CAD-4 diffractometer (purchased under Grant DPT/TBAG1 to the Scientific and Technical Research Council of Turkey) of the Physics Engineering Department, Hacettepe University, Turkey.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1057). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 529–531

2-Salicylideneamino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile

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(Received 13 June 1997; accepted 20 October 1997)

Abstract

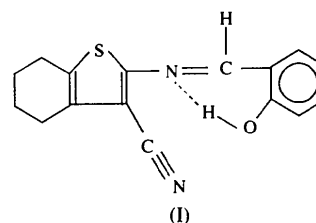
Molecules of the title compound, $C_{16}H_{14}N_2OS$, are nearly planar. Each molecule contains an intramolecular $O \cdots N$ hydrogen bond [2.626 (2) Å].

Comment

Schiff bases have been used widely as ligands in the formation of transition metal complexes. Many such complexes have been structurally characterized, but only a relatively small number of free Schiff bases have been similarly characterized (Calligaris & Randaccio, 1987). *N*-Substituted salicylaldimines have been found to display thermochromism and photochromism in the solid state by proton transfer from the hydroxy O atom to the imine N atom, which may be reversible (Moustakali *et al.*, 1978; Hadjoudis *et al.*, 1987; Xu *et al.*, 1994). The

charge transport occurs through overlapping intermolecular π orbitals with proton transfer; the proton transfer may also be a basis for the development of molecular switches (Xu *et al.*, 1994). Interest in photochromic compounds has been increasing ever since the potential applications of photochromic materials were realised in various areas, such as the control and measurement of radiation intensity, optical computers and display systems (Dürr, 1989; Dürr & Bouas-Laurent, 1990).

Our structural investigation of the Schiff bases (Elerman *et al.*, 1991, 1992, 1994, 1995, 1997; Elmali *et al.*, 1995; Kevran *et al.*, 1996; Elmali & Elerman, 1997) have led us to examine the title compound, (I). The molecular geometry is illustrated in Fig. 1.



On the basis of some thermochromic and photochromic Schiff base compounds, it was proposed that molecules exhibiting thermochromism are planar, while those exhibiting photochromism are non-planar (Moustakali *et al.*, 1978), and that planarity of the molecule facilitates proton transfer through the hydrogen bond in the ground state (Bregman, Leiserowitz & Schmidt, 1964; Bregman, Leiserowitz & Osaki, 1964). In agreement with the above conclusions, the present molecule (excluding C13 and C14) is planar [with the largest deviation from planarity being 0.346 (2) Å for atom C13] and thermochromic (Kabak, 1998). There is a strong intramolecular hydrogen bond $O1 \cdots N1$ [2.626 (2) Å] in which the H atom is bonded to the O atom (the H1O atom was located from a difference Fourier map at the end of the refinement process as a small positive electron density). The sum of the van der Waals radii of O and N (3.07 Å; Bondi, 1964) is significantly longer than the $O \cdots N$ hydrogen-bond length, which is similar to the corresponding bond lengths in *N*-(2-hydroxyphenyl)salicylaldimine [2.625 (7) Å; Elerman *et al.*, 1995], 2,2'-azinodimethyldiphenol [2.611 (6) Å; Xu *et al.*, 1994] and bis-*N,N'*-*p*-chlorosalicylideneamine-1,2-diaminobenzene [2.615 (6) Å; Elerman *et al.*, 1994]. The $O1-H1O$ and $H1O \cdots N1$ distances are 0.88 (3) and 1.83 (3) Å, respectively. The $O1-H1O \cdots N1$ angle is 150 (2)°. The unit cell and hydrogen-bonding scheme are shown in Fig. 2. Apart from the intramolecular hydrogen bond, there is also an intermolecular $C-H \cdots N$ contact, $C7 \cdots N2(\frac{1}{2} - x, \frac{1}{2} + y, z)$ 3.401 (3) Å. Such $C-H \cdots N$ contacts are thought to represent significant polar attractions (Berkovitch-Yellin & Leiserowitz, 1984) contributing to the overall packing.