Acta Crystallographica Section E
Structure Reports Online

ISSN 1600-5368

{3-[4-(*N,N*-Dimethylamino)phenyl]-1-(4-methylphenyl)-3-(phenylsulfanyl)propylidene}semicarbazide

Sivaperuman Saravanan and Shanmugam Muthusubramanian*

Department of Organic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India

Correspondence e-mail: muthumanian2001@yahoo.com

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.101
Data-to-parameter ratio = 14.6

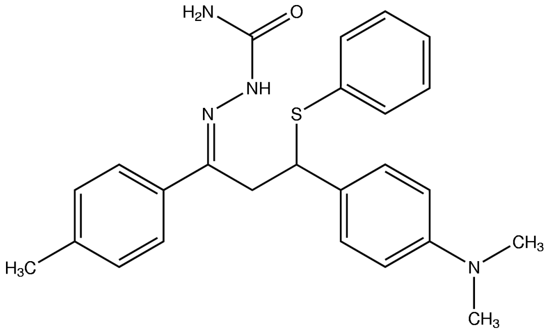
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 27 August 2004
Accepted 23 September 2004
Online 30 September 2004

In the title compound, $C_{25}H_{28}N_4OS$, the benzene rings are nearly perpendicular to the central C—C—C—S linkage, whereas the semicarbazide plane forms a dihedral angle of 67.7 (1)° with the central linkage. In the crystal structure, inversion-related molecules exist as N—H···O hydrogen-bonded dimers.

Comment

Studies on 1,2,3-selenadiazoles and 1,2,3-thiadiazoles have attracted much attention not only due to their pharmacological properties, such as antifungal (Jalilian *et al.*, 2003) and antibacterial activities (Lalezari *et al.*, 1974), but also due to their wide-ranging utility as synthons in organic synthesis (Arsenyan *et al.*, 2002; Morzherin *et al.*, 2003). In a continuation of our work on the synthesis and characterization of 1,2,3-selenadiazoles and 1,2,3-thiadiazoles (Muthusubramanian *et al.*, 1997; Saravanan & Muthusubramanian, 2004), we planned to synthesize more 1,2,3-selena/thiadiazoles. In this regard, we prepared several semicarbazones of 1,3-diaryl-3-phenylthiopropan-1-ones, including the title compound, {3-[4-(*N*,*N*-dimethylamino)phenyl]-1-(4-methylphenyl)-3-(phenylsulfanyl)propylidene}semicarbazide, (I). The reaction of these ketones with semicarbazide hydrochloride is very sensitive in the sense that heating the reaction mixture leads to elimination of the phenylsulfanyl group, and hence the reaction was carried out at room temperature in dioxane in the presence of the phase-transfer catalyst tetrabutylammonium bromide.



(I)

In the title molecule, the phenylsulfanyl (C20–C25), methylphenyl (C2–C7), dimethylaminophenyl (C12–C17) and semicarbazide (N1–N3/O1/C9) groups make dihedral angles of 87.9 (1), 88.2 (1), 83.0 (1) and 67.7 (1)°, respectively, with the central C8—C10—C11—S1 linkage. The C8—C10—C11—C12 and C8—C10—C11—S1 torsion angles of 72.3 (2) and −165.8 (1)°, respectively, show that the imino C atom is nearly *gauche* to the C12-aryl ring and *anti* to the phenylsulfanyl ring.

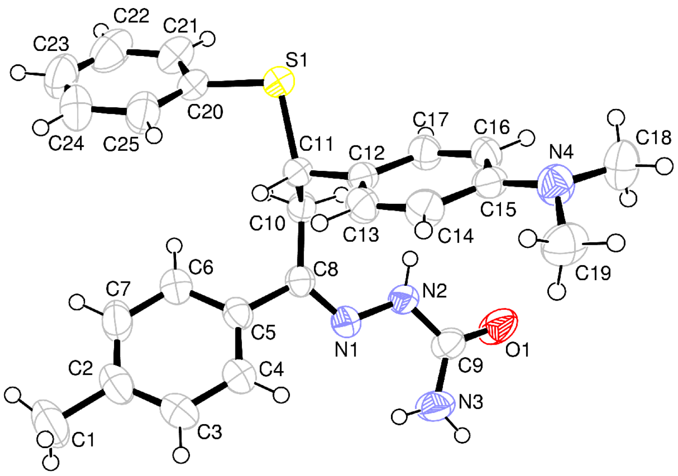


Figure 1
A view of the molecule of of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

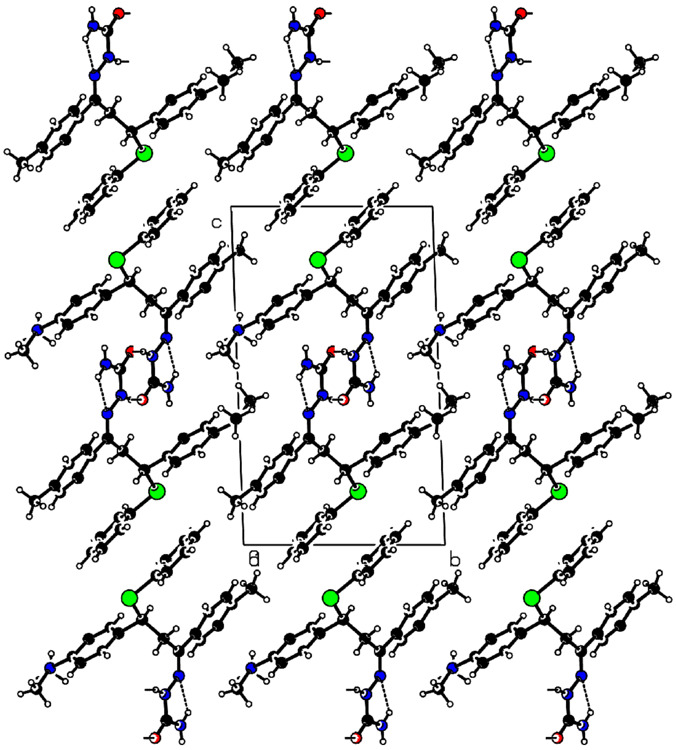


Figure 2
Packing of the molecules, viewed down the *a* axis, showing the dimer formation. Hydrogen bonds are indicated by dashed lines.

The close approach of atoms H2 and H10*B* (H2$\cdots$H10*B* = 1.97 Å) results in the widening and narrowing of angles N1—C8—10 [127.6 (2)°] and N1—C8—C5 [113.9 (2)°] from the normal 120°.

In the crystalline state, inversion-related molecules exist as N2—H2$\cdots$O1^{i} and C10—H10B$\cdots$O1^{i} hydrogen-bonded dimers (Table 1). One of the amino H atoms, H3*B*, is involved in an intramolecular N3—H3*B*$\cdots$N1 hydrogen bond, whereas the other atom, H3*A*, is not involved in any hydrogen bond (Fig. 2).

Experimental

To a solution of 3-[4-(dimethylamino)phenyl]-1-(4-methylphenyl)-3-(phenylsulfanyl)propan-1-one (1.88 g, 0.005 mol), semicarbazide hydrochloride (4.46 g) and sodium acetate (3.28 g) in a dioxane–water mixture (50 ml, 3:2 *v*/*v*), a catalytic amount of the phase-transfer catalyst tetrabutylammonium bromide was added. The reaction mixture was stirred at room temperature for 3 d, then extracted with chloroform and evaporated to dryness. The insoluble ethyl acetate portion was crystallized from ethanol to give the title compound (m.p. 445 K). IR (KBr, ν, cm^{-1}): 3508, 3392, 1682, 1562; ^{1}H NMR (CDCl$_3$, p.p.m.): 9.33 (*s*, 1H), 8.13 (*s*, 2H), 7.39 (*d*, 2H, *J* = 8.1 Hz), 7.12–7.19 (*m*, 5H), 6.56 (*d*, 2H, *J* = 8.7 Hz), 6.29 (*s*, 2H), 4.33 (*t*, 1H), 3.65 (*m*, 2H), 2.86 (*s*, 6H), 2.33 (*s*, 3H); ^{13}C NMR (CDCl$_3$, p.p.m.): 157.70, 149.89, 145.40, 138.17, 135.15, 134.62, 131.71, 129.04, 128.98, 128.40, 128.10, 127.17, 126.45, 112.20, 79.14, 50.18, 33.21, 21.15.

Crystal data

$C_{25}H_{28}N_4OS$
M_r = 432.57
Triclinic, $P\overline{1}$
a = 6.804 (5) Å
b = 10.531 (4) Å
c = 17.278 (5) Å
α = 88.96 (5)°
β = 79.24 (3)°
γ = 73.51 (2)°
V = 1165.4 (10) Å^3
Z = 2
D_x = 1.233 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 11.2–14.1°
μ = 0.16 mm^{-1}
T = 293 (2) K
Needle, colourless
0.35 × 0.25 × 0.15 mm

Data collection

Nonius MACH3 four-circle diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.975, $T_{\max}$ = 0.982
4584 measured reflections
4083 independent reflections
3120 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.014
$\theta_{\max}$ = 25.0°
$h = -7 \rightarrow 8$
$k = -1 \rightarrow 12$
$l = -20 \rightarrow 20$
3 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.101
S = 1.03
4083 reflections
280 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 0.3387P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.19 e Å^{-3}
$\Delta\rho_{\min}$ = −0.22 e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$\cdots$O1^{i}	0.86	2.03	2.843 (3)	157
C10—H10*B*$\cdots$O1^{i}	0.97	2.38	3.333 (2)	169
N3—H3*B*$\cdots$N1	0.86	2.24	2.606 (2)	105

Symmetry code: (i) $2 - x, 1 - y, 1 - z$.

All H atoms were placed in calculated positions (N—H = 0.86 Å and C—H = 0.93–0.98 Å) and included in the refinement in a riding-model approximation, with $U_{\rm iso}$ values constrained to be 1.5$U_{\rm eq}$ of the carrier atom for methyl H atoms and 1.2$U_{\rm eq}$ for the remaining H atoms.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

The authors thank the DST, New Delhi, for assistance under the IRHPA program for the NMR facility. SS is grateful to the CSIR, New Delhi, for the award of a Junior Research Fellowship.

References

Arsenyan, P., Oberte, K., Pudova, O. & Lukevics, E. (2002). *Chem. Heterocycl. Compd.* **38**, 1437–1447.

Enraf–Nonius (1994). *CAD*-4 *EXPRESS*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Harms, K. & Wocadlo, S (1995). *XCAD*4. University of Marburg, Germany.

Jalilian, A. R., Sattari, S., Bineshmarvasti, M., Daneshtalab, M. & Shafiee, A. (2003). *Il Farmaco*, **58**, 63–68.

Lalezari, I., Shafiee, A. & Yazdany, S. (1974). *J. Pharm. Sci.* **63**, 628–629.

Morzherin, Yu. Yu., Glukhareva, T. V. & Bakulev, V. A. (2003). *Chem. Heterocycl. Compd*, **39**, 679–706.

Muthusubramanian, S., Parvathi, K. & Sivasubramanian. S. (1997). *Indian J. Heterocycl. Chem.* **6**, 227–228.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Saravanan, S. & Muthusubramanian, S. (2004). *Phosphorus Sulfur Silicon Relat. Elem.* In the press.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (1999). *PLATON for Windows*. Utretcht University, The Netherlands.