Crystal and molecular structure of Thiadiazole derivatives 5-[(4-Methoxybenzyl)sulfanyl]-2-methyl-1,3,4-thiadiazole.

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ABSTRACT: The role of hydrogen bonds was found to be essential for the stabilization of conformationally strained molecules as well as for the packing density of such molecules in a crystal.The title molecule, $C_{11}H_{12}N_2OS_2$, is twisted with a dihedral angle of 83.63 (12)° between the 1,3,4-thiadiazole and benzene rings. All H atoms were positioned geometrically and allowed to ride on their parent atoms, with d(C—H) = 0.93 Å for aromatic, 0.97 Å for $CH_2$and 0.96 Å for CH_3 atoms. The U_{iso}(H) values were constrained to be $1.5U_{\mathrm{eq}}$(C) for methyl H atoms and $1.2U_{\mathrm{eq}}$(C) for the remaining H atoms. A rotating group model was used for the methyl groups.The methoxy group deviates slightly from the attached benzene ring, with a C-C-O-C torsion angle of 4.2 (4)°. In the crystal, molecules are linked by weak C-H···N interactions and stacked along the *c* axis.

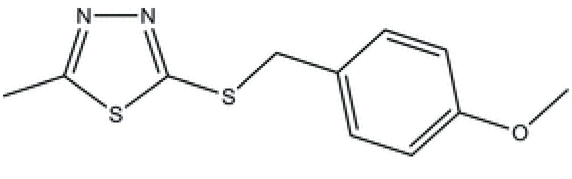
Key Words : *Torsion Angle *Mean σ(C-C) = 0.004 **R* factor = 0.052
wR factor = 0.118Data-to-parameter ratio = 19.2

Introduction :

Thiadiazole are a class of heterocyclic compounds having a five membered ring. They occur in nature and are predominant among all types of pharmaceuticals, agrochemicals and veterinary products (El-Sabbagh et al., 2009). The amino and mercapto groups in thiadiazole are readily-accessible nucleophilic centers. 1,3,4-Thiadiazole exhibit a wide spectrum of biological activities (Bernard et al., 1985). Due to the presence of the –N—C—S moiety (Kalluraya et al., 2004), they are found to be used as antibacterial, antimicrobial and anti-inflammatory agents (Chandrakantha et al., 2010). Antibacterial and antifungal (Isloor et al., 2010) activities of the azoles are most widely studied and azoles are also used as antimicrobial agents. Herein we report the crystal structure of the title 1,3,4-thiadiazole derivative, (I).

The molecule of (I) (Fig. 1) is twisted with a dihedral angle between the 1,3,4-thiadiazole and benzene rings being 83.63 (12)°. Atoms C3, S2, C4 and C5 lie nearly on the same plane with r.m.s. 0.0517 (5) Å and the torsion angle C3–S2–C4–C5 = 172.25 (18)°. The mean plane through C3/S2/C4/C5 makes the dihedral angles of 9.02 (15) and 75.92 (16)° with the 1,3,4-thiadiazole and benzene rings, respectively. The methoxy group is slightly deviated with respect to the attached benzene ring with the torsion angle C11–O1–C8–C9 = 4.2 (4)°. The bond distances are of normal values (Allen et al., 1987) and are comparable with the related structure (Wang et al., 2010).

Experimental :



The title compound was synthesized by adding 4-methoxybenzylbromide (3.02 g, 0.0151 mol) dropwise to a stirred solution of 5-methyl-1,3,4-thiadiazole-2-thiol (2.00 g, 0.0151 mol) and anhydrous potassiumcarbonate (4.16 g, 0.03 mol) in dry acetonitrile (50 ml) at room temperature and the reaction mixture was stirred at room temperature for 5 h. After the completion of reaction, the reaction mixture was filtered and the filtrate was concentrated. The crude product was recrystallized with hot ethanol to afford the title compound as yellow solid (2.00 g, yield 57%). Yellow plate-shaped single crystals of the title compound suitable for *x*-ray structure determination were recrystalized from ethanol by the slow evaporation of the solvent at room temperature after several days (m.p. 413–415 K).

Experimental

Crystal data

- **$C_{11}H_{12}N_2OS_2$**
- **$M_r = 255.35$**
- **Monoclinic, $P\ 2_1\ /c$**
- **$a = 14.5765\ (4)$ Å**
- **$b = 8.7656\ (3)$ Å**
- **$c = 9.5769\ (3)$ Å**
- **$\beta = 96.587\ (1)°$**
- **$V = 1288.17\ (7)$ Å^3**
- **$Z = 4$**
- **Mo $K\alpha$ radiation**
- **$\mu = 0.46$ mm^{-1}**
- **$T = 296$ K**
- **0.25 × 0.19 × 0.03 mm**

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with d(C—H) = 0.93 Å for aromatic, 0.97 Å for $CH_2$and 0.96 Å for CH_3 atoms. The U_{iso}(H) values were constrained to be $1.5U_{eq}$(C) for methyl H atoms and $1.2U_{eq}$(C) for the remaining H atoms. A rotating group model was used for the methyl groups.

Fig shows the molecular structure of the title compound showing 40 % probability displacement ellipsoids .

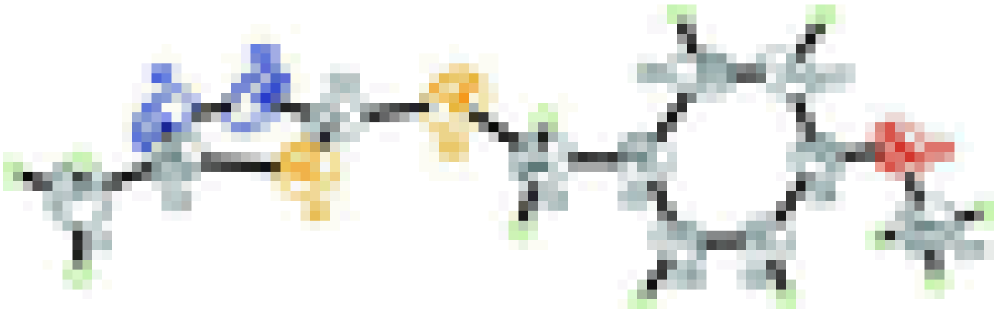
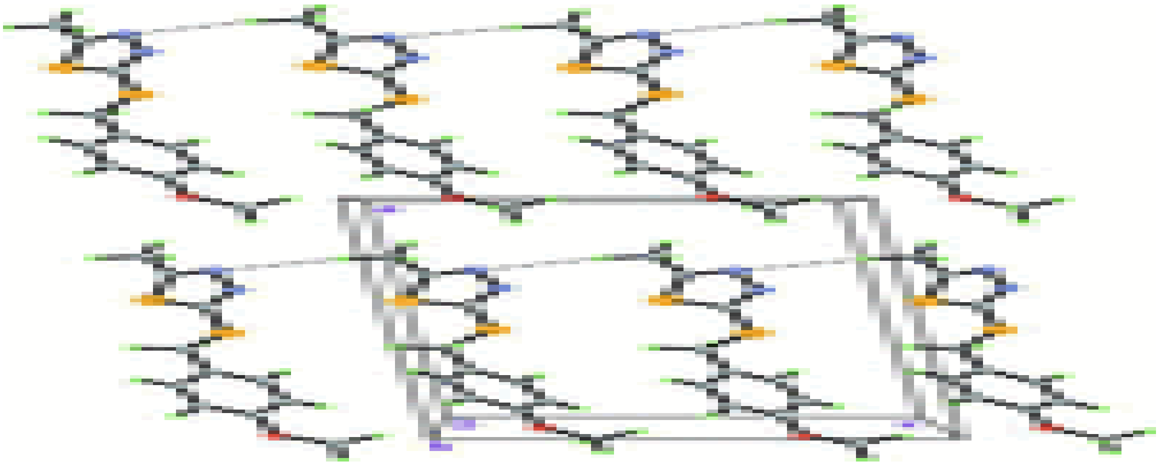


Figure shows the crystal packing of the title compound viewed along the b -axis C-H....N weak interactions

As shown as dashed lines



Data collection : 5-[(4-Methoxybenzyl)sulfanyl]-2-methyl-1,3,4-thiadiazole

C11H12N2OS2

F(000) = 528

- $C_{11}H_{12}N_2OS_2$
- M_r = 255.35
- Monoclinic, $P\ 2_1/c$
- a = 14.5765 (4) Å
- b = 8.7656 (3) Å
- c = 9.5769 (3) Å
- β = 96.587 (1)°
- V = 1288.17 (7) $Å^3$
- Z = 4
- Mo Kα radiation
- μ = 0.46 mm^{-1}
- T = 296 K
- 0.25 × 0.19 × 0.03 mm

- **11429 measured reflections**
- 2828 independent reflections
- 1660 reflections with $I > 2\sigma(I)$

Melting point = 413–415 K

Dx = 1.349 Mg m−3

Hall symbol: -P 2ybc Mo Kα radiation, λ = 0.71073 Å

θ = 2.7–27.5°

β = 96.477 (1)° T = 296 K

V = 1242.16 (7) Å3 Plate, yellow

Z = 4 0.25 × 0.19 × 0.03 mm

Refinement:

Bruker APEXII CCD area-detector

diffractometer 2828 independent reflections

Radiation source: sealed tube 1660 reflections with I > 2σ(I)

Graphite monochromator Rint = 0.040

ϕ and ω scans θmax = 27.5°, θmin = 2.7°

Absorption correction: multi-scan

(SADABS; Bruker, 2005) h = −19→19

Tmin = 0.907, Tmax = 0.987 k = −11→11

11429 measured reflections l = −12→12

Refinement on F2 Primary atom site location: structure-invariant direct methods

Least-squares matrix: full Secondary atom site location: difference Fourier map

R[F2 > 2σ(F2)] = 0.052 Hydrogen site location: inferred from neighbouring sites

wR(F2) = 0.118 H-atom parameters constrained

S = 1.02 w = 1/[σ2(Fo2) + (0.0454P)2 + 0.2899P]

where P = (Fo2 + 2Fc2)/3

2828 reflections (Δ/σ)max = 0.001

147 parameters Δρmax = 0.23 e Å−3

0 restraints Δρmin = −0.19 e Å−3

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

Refinement. Refinement of F2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F2, conventional R-factors R are based on F, with F set to zero for negative F2. The threshold expression of F2 > σ(F2) is used only for calculating R-factors(gt)etc. and is not relevant to the choice of reflections for refinement. R-factors based on F2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å2)

	x	y	z	U_{iso}*/U_{eq}
S1	0.43447 (5)	0.19481 (8)	0.95596 (7)	0.0631 (2)
S2	0.56474 (5)	0.40517 (9)	0.81756 (8)	0.0805 (3)
O1	0.99330 (14)	0.4254 (2)	0.7932 (2)	0.0899 (7)
N1	0.30610 (16)	0.3239 (3)	0.8041 (2)	0.0770 (7)
N2	0.38487 (18)	0.3952 (3)	0.7726 (2)	0.0795 (7)
C1	0.24763 (19)	0.1218 (4)	0.9455 (3)	0.0849 (9)
H1A	0.1893	0.1624	0.9098	0.127*
H1B	0.2534	0.1234	1.0447	0.127*
H1C	0.2529	0.0178	0.9141	0.127*
C2	0.32087 (18)	0.2174 (3)	0.8958 (2)	0.0616 (7)
C3	0.45726 (18)	0.3383 (3)	0.8427 (2)	0.0609 (7)
C4	0.63995 (18)	0.2718 (3)	0.9180 (3)	0.0672 (7)
H4A	0.6353	0.2848	1.0159	0.081*
H4B	0.6239	0.1665	0.8925	0.081*
C5	0.73488 (17)	0.3071 (3)	0.8867 (2)	0.0581 (7)
C6	0.7820 (2)	0.4335 (3)	0.9444 (3)	0.0697 (8)
H6A	0.7551	0.4956	1.0062	0.084*
C7	0.8673 (2)	0.4688 (3)	0.9122 (3)	0.0738 (8)
H7A	0.8977	0.5539	0.9528	0.089*
C8	0.90874 (18)	0.3794 (3)	0.8200 (3)	0.0624 (7)
C9	0.86360 (19)	0.2522 (3)	0.7635 (3)	0.0678 (7)
H9A	0.8909	0.1892	0.7029	0.081*
C10	0.77752 (18)	0.2183 (3)	0.7970 (3)	0.0653 (7)
H10A	0.7475	0.1324	0.7573	0.078*
C11	1.0358 (2)	0.3427 (5)	0.6936 (4)	0.1167 (14)

H11A	1.0964	0.3813	0.6905	0.175*
H11B	1.0014	0.3548	0.6046	0.175*
H11C	1.0385	0.2356	0.7180	0.175*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0756 (5)	0.0557 (4)	0.0557 (4)	0.0085 (3)	−0.0024 (3)	0.0090 (3)
S2	0.0880 (6)	0.0761 (6)	0.0793 (5)	0.0158 (4)	0.0181 (4)	0.0313 (4)
O1	0.0779 (14)	0.0861 (16)	0.1076 (16)	−0.0229 (11)	0.0186 (12)	−0.0254 (12)
N1	0.0787 (17)	0.0942 (19)	0.0594 (14)	0.0339 (14)	0.0139 (12)	0.0159 (14)
N2	0.0849 (17)	0.0896 (18)	0.0665 (15)	0.0385 (15)	0.0200 (13)	0.0277 (14)
C1	0.079 (2)	0.094 (2)	0.079 (2)	−0.0025 (18)	−0.0034 (16)	0.0020 (18)
C2	0.0744 (18)	0.0651 (18)	0.0449 (14)	0.0152 (14)	0.0056 (13)	−0.0067 (13)
C3	0.0806 (18)	0.0570 (17)	0.0466 (14)	0.0229 (14)	0.0137 (13)	0.0045 (12)
C4	0.0779 (19)	0.0640 (18)	0.0595 (16)	0.0065 (14)	0.0061 (14)	0.0151 (14)
C5	0.0708 (17)	0.0520 (16)	0.0507 (14)	0.0007 (13)	0.0035 (13)	0.0073 (13)
C6	0.099 (2)	0.0566 (18)	0.0563 (16)	−0.0032 (16)	0.0208 (15)	−0.0093 (14)
C7	0.099 (2)	0.0593 (18)	0.0631 (17)	−0.0209 (16)	0.0091 (16)	−0.0141 (15)
C8	0.0659 (17)	0.0571 (17)	0.0626 (17)	−0.0049 (14)	0.0002 (13)	−0.0044 (14)
C9	0.0701 (18)	0.0569 (17)	0.0758 (18)	0.0007 (14)	0.0062 (14)	−0.0168 (15)
C10	0.0701 (18)	0.0512 (17)	0.0726 (18)	−0.0057 (13)	−0.0011 (14)	−0.0122 (14)
C11	0.092 (2)	0.105 (3)	0.162 (4)	−0.014 (2)	0.051 (3)	−0.037 (3)

Geometric parameters (Å, º)

S1—C3	1.723 (3)	C4—H4B	0.9700
S1—C2	1.725 (3)	C5—C10	1.371 (3)
S2—C3	1.734 (3)	C5—C6	1.386 (4)
S2—C4	1.814 (3)	C6—C7	1.367 (4)
O1—C8	1.365 (3)	C6—H6A	0.9300
O1—C11	1.410 (3)	C7—C8	1.382 (4)
N1—C2	1.288 (3)	C7—H7A	0.9300
N1—N2	1.383 (3)	C8—C9	1.373 (4)
N2—C3	1.300 (3)	C9—C10	1.380 (3)

C1—C2	1.488 (4)	C9—H9A	0.9300
C1—H1A	0.9600	C10—H10A	0.9300
C1—H1B	0.9600	C11—H11A	0.9600
C1—H1C	0.9600	C11—H11B	0.9600
C4—C5	1.500 (3)	C11—H11C	0.9600
C4—H4A	0.9700		

C3—S1—C2	87.33 (13)	C10—C5—C4	121.5 (2)
C3—S2—C4	102.99 (12)	C6—C5—C4	121.2 (2)
C8—O1—C11	118.1 (2)	C7—C6—C5	121.3 (2)
C2—N1—N2	113.2 (2)	C7—C6—H6A	119.4
C3—N2—N1	112.1 (2)	C5—C6—H6A	119.4
C2—C1—H1A	109.5	C6—C7—C8	120.7 (3)
C2—C1—H1B	109.5	C6—C7—H7A	119.7
H1A—C1—H1B	109.5	C8—C7—H7A	119.7
C2—C1—H1C	109.5	O1—C8—C9	125.0 (2)
H1A—C1—H1C	109.5	O1—C8—C7	116.2 (2)
H1B—C1—H1C	109.5	C9—C8—C7	118.8 (3)
N1—C2—C1	123.7 (3)	C8—C9—C10	119.8 (3)
N1—C2—S1	113.5 (2)	C8—C9—H9A	120.1
C1—C2—S1	122.8 (2)	C10—C9—H9A	120.1
N2—C3—S1	113.7 (2)	C5—C10—C9	122.2 (2)
N2—C3—S2	120.7 (2)	C5—C10—H10A	118.9
S1—C3—S2	125.53 (16)	C9—C10—H10A	118.9
C5—C4—S2	106.83 (17)	O1—C11—H11A	109.5
C5—C4—H4A	110.4	O1—C11—H11B	109.5
S2—C4—H4A	110.4	H11A—C11—H11B	109.5
C5—C4—H4B	110.4	O1—C11—H11C	109.5
S2—C4—H4B	110.4	H11A—C11—H11C	109.5
H4A—C4—H4B	108.6	H11B—C11—H11C	109.5
C10—C5—C6	117.3 (2)		

C2—N1—N2—C3	0.2 (3)	S2—C4—C5—C6	76.6 (3)
N2—N1—C2—C1	−178.9 (2)	C10—C5—C6—C7	0.5 (4)
N2—N1—C2—S1	0.9 (3)	C4—C5—C6—C7	−177.7 (2)
C3—S1—C2—N1	−1.3 (2)	C5—C6—C7—C8	0.4 (4)
C3—S1—C2—C1	178.5 (2)	C11—O1—C8—C9	4.2 (4)
N1—N2—C3—S1	−1.3 (3)	C11—O1—C8—C7	−176.3 (3)
N1—N2—C3—S2	178.12 (18)	C6—C7—C8—O1	179.1 (2)
C2—S1—C3—N2	1.5 (2)	C6—C7—C8—C9	−1.4 (4)
C2—S1—C3—S2	−177.88 (18)	O1—C8—C9—C10	−179.1 (3)
C4—S2—C3—N2	−171.8 (2)	C7—C8—C9—C10	1.5 (4)
C4—S2—C3—S1	7.5 (2)	C6—C5—C10—C9	−0.4 (4)
C3—S2—C4—C5	172.25 (18)	C4—C5—C10—C9	177.8 (2)
S2—C4—C5—C10	−101.5 (3)	C8—C9—C10—C5	−0.6 (4)

Hydrogen Bonding

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*B*···N1^{i}	0.96	2.59	3.532 (4)	164

Symmetry code: (i) *x*, −*y*+1/2, *z*+1/2

Conclusion:

The title molecule, $C_{11}H_{12}N_2OS_2$, is twisted with a dihedral angle of 83.63 (12)° between the 1,3,4-thiadiazole and benzene rings. The methoxy group deviates slightly from the attached benzene ring, with a C-C-O-C torsion angle of 4.2 (4)°. In the crystal, molecules are linked by weak C-H···N interactions.

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