Crystal Structure of (2E)-3-(2-Thienyl)acrylic acid-benzene-1,2-diamine

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The title compound, (2E)-3-(2-thienyl)acrylic acid-benzene-1,2-diamine, was synthesized by the reaction of 1,2-diaminobenzene and 3-(2-thienyl)acrylic acid in a dioxane solution. The compound crystallizes in the orthorhombic space group *Pbcn*; *a* = 24.610(5) Å, *b* = 7.588(5) Å, *c* = 11.289(5) Å, *V* = 2108.1(17) Å³ and *Z* = 8. The final *R* value is 0.047. The thiophene and benzene ring are each essentially planar. The benzene-1,2-diamine moiety in the title compound has a rotation axis that passes through the mid point of the bonds C8–C8a and C10–C10a. The crystal packing is stabilized by intermolecular N–H... and O–H...N hydrogen-bonding interactions.

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Heterocyclic compounds generally show versatile pharmacological activities, such as antitumor, diuretics, fungicides, bactericides, antihelmintic, antiallergic, vasodilator, antihistaminic, anti-ulcer and local analgesic.^{1–3} We here report

on the crystal structure of (2E)-3-(2-thienyl)acrylic acid-benzene-1,2-diamine, based on our studies.

A mixture of 1,2-diaminobenzene (1.08 g; 10 mmol) and 3-(2-thienyl)acrylic acid (1.54 g; 10 mmol) in dioxane (10 ml) was heated under reflux for 3 h. The mixture was then cooled and the volatiles were removed by vacuo (Fig. 1). The residue was crystallized from an EtOH/Et₂O (3:1) mixture. Yield: 1.86 g, 71%. M.p.: 391–392 K.

¹H-NMR (D₂O): δ 6.10 (d, HC=, 1H), δ 6.75 (m, Ph-H and NH₂^{+1/2}, 9H), δ 6.91 (t, thienyl, 1H), δ 7.14 (d, thienyl, 1H), δ 7.29

Fig. 1 Chemical scheme of the title compound.

Table 1 Crystal and experimental data

Formula: C₇H₆O₂S·(C₆H₈N₂)
Formula weight = 208.26
Crystal system: orthorhombic
Space group: *Pbcn*; *Z* = 8
a = 24.610(5) Å
b = 7.588(5) Å
c = 11.289(5) Å
V = 2108.1(17) Å³
*D*_x = 1.312 g cm^{−3}
μ(Mo *K*_α) = 0.28 mm^{−1}
T = 293(2) K
Crystal size = 0.66 × 0.52 × 0.38 mm
Radiation: Mo *K*_α
R = 0.047
*R*_w = 0.147
No. of unique data measured = 2277
No. of observed data with [*I* ≥ 2σ(*I*)] = 1756
No. of parameters = 140
Goodness-of-fit = 1.05
(Δρ)_{max} = 0.37 e Å^{−3}
(Δρ)_{min} = −0.37 e Å^{−3}
Measurements: STOE IPDS 2 diffractometer
Program system: X-AREA
Structure determination: SIR97
Refinement: SHELXL97

CCDC 626235 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2 Final atomic coordinates and equivalent isotropic thermal displacement parameters for non-hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
S1	0.21661 (2)	0.32011 (9)	0.45512 (5)	0.0771 (2)
O1	0.42432 (5)	0.4007 (2)	0.59672 (12)	0.0693 (5)
O2	0.37829 (5)	0.4720 (2)	0.75866 (12)	0.0670 (5)
C1	0.14870 (10)	0.3243 (3)	0.4744 (2)	0.0790 (8)
C2	0.13336 (9)	0.3688 (3)	0.5839 (3)	0.0777 (7)
C3	0.17744 (7)	0.4042 (3)	0.6654 (2)	0.0660 (6)
C4	0.22806 (7)	0.3830 (2)	0.59908 (16)	0.0558 (5)
C5	0.28167 (7)	0.4098 (2)	0.64720 (16)	0.0564 (5)
C6	0.32852 (7)	0.3829 (3)	0.59242 (17)	0.0598 (5)
C7	0.38095 (7)	0.4192 (2)	0.64811 (15)	0.0550 (5)
N1	0.52999 (7)	1.4105 (2)	0.14526 (13)	0.0552 (5)
C8	0.51465 (11)	0.9321 (3)	0.1976 (4)	0.0950 (12)
C9	0.52890 (8)	1.0881 (3)	0.1454 (2)	0.0700 (7)
C10	0.51435 (6)	1.2470 (2)	0.19650 (14)	0.0519 (5)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* (a_i a_j).$$

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Fig. 2 ORTEP-3 view of the title compound, with the atom-numbering scheme and 30% probability displacement ellipsoids.

Table 3 Bond lengths (Å) and bond angles (°)

S1-C1	1.686(3)	O2-C7	1.312(2)
S1-C4	1.717(2)	N1-C10	1.422(2)
O1-C7	1.223(2)	C1-C2	1.336(4)
C2-C3	1.448(4)	C8-C9	1.368(4)
C3-C4	1.462(3)	C8-C8 [±]	1.386(6)
C4-C5	1.441(3)	C9-C10	1.384(3)
C5-C6	1.324(3)	C10-C10 [±]	1.399(2)
C6-C7	1.462(3)		
C1-S1-C4	92.02(10)	O2-C7-C6	115.00(15)
S1-C1-C2	113.86(18)	O1-C7-O2	121.99(16)
S1-C4-C3	112.05(13)	N1-C10-C9	121.37(16)
S1-C4-C5	123.11(13)	N1-C10-C10 [±]	119.20(14)
O1-C7-C6	123.01(16)	C1-C2-C3	115.0(2)
C2-C3-C4	107.0(2)	C8 [±] -C8-C9	120.1(2)
C3-C4-C5	124.85(17)	C8-C9-C10	120.5(2)
C4-C5-C6	126.82(17)	C9-C10-C10 [±]	119.37(16)
C5-C6-C7	122.60(17)		

Symmetry codes: (i) 1-x, y, 1/2, -z.

(d, thienyl, 1H), δ 7.40 (d, HC=, 1H).

¹³C-NMR (CDCl₃): δ 115.00, 117.75, 117.95, 128.95, 129.94, 132.12, 135.38, 137.17, 139.38, 177.76. Anal. calcd. for C₁₃H₁₄N₂O₂S: C, 59.54, H, 5.34, N, 10.68, S, 13.21%. Found: C, 58.74, H, 5.15, N, 10.25, S, 13.18%.

The crystallographic details are given in Table 1. The structure was solved by direct methods and refined by least squares on F_{obs}^2 by using the SIR97 and SHELXL97 programs, respectively. The H atoms of the hydroxyl and amino groups were found from a difference Fourier map and refined freely.

Table 4 Hydrogen-bonding geometry (Å, °)

D-H...A	D-H	H...A	D...A	D-H...A
N1-H1A...O1 ⁱ	0.96(2)	2.00(2)	2.955(3)	174(2)
N1-H1B...O1 ⁱⁱ	0.71(2)	2.35(2)	3.019(3)	157(2)
O2-H10...N1 ⁱⁱⁱ	0.76(3)	1.90(3)	2.658(3)	173(3)

Symmetry codes: (i) 1-x, 1+y, 1/2-z; (ii) x, 2-y, -1/2+z; (iii) 1-x, 2-y, 1-z.

The other H atoms were positioned geometrically, with C-H = 0.93 Å, and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

The title molecule is shown in Fig. 2; the final atomic coordinates and the equivalent isotropic thermal parameters for non-hydrogen atoms are listed in Table 2, with selected bond lengths and bond angles listed in Tables 3. The molecule has a two-fold rotation axis located at the center of the benzene ring in the benzene-1,2-diamine moiety. In the crystal structure of the title compound, the bond lengths and angles are normal,^{4,6} with the exception of the bond lengths S1-C1 [1.686(3)Å], S1-C4 [1.717(2)Å], C3-C4 [1.462(3)Å], C1-C2 [1.337(4)Å] and C2-C3 [1.447(4)Å]. The benzene-1,2-diamine moiety in the title compound has a rotation axis that passes through the mid point of the bonds C8-C8a and C10-C10a.

The (2E)-3-(2-thienyl)arctic acid and the benzene-1,2-diamine moieties are almost planar, with maximum deviations of 0.033(2), -0.027(2) and -0.049(2)Å for O2, C3 and C6 in the first moiety, and -0.013(2) and 0.014(2)Å for C10 and N1 in the second moiety, respectively. The dihedral angle between the planes of these two moieties is 80.94(11)°. The crystal structure of title compound is stabilized by intermolecular N-H...O and O-H...N interactions; details are listed in Table 4.

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