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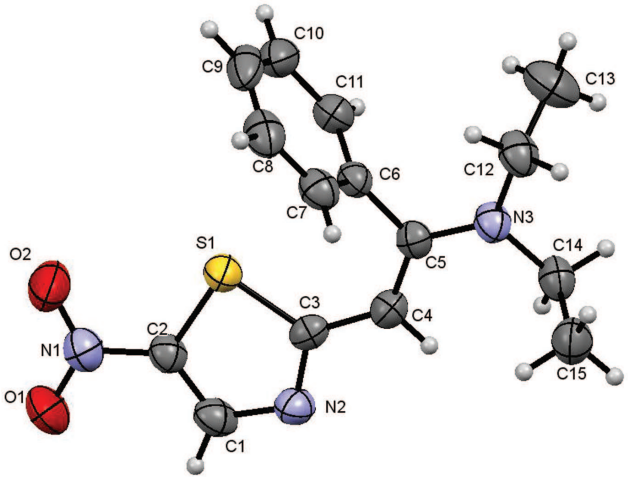
Nur Farahin Pairan, Noor Azilah Mohd Kasim, Bohari M. Yamin and Noor Aisyah Ahmad Shah*

Crystal structure of (*E*)-*N*,*N*-diethyl-2-(5-nitrothiazol-2-yl)-1-phenylethen-1-amine, $C_{15}H_{17}N_3O_2S$



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Abstract

$C_{15}H_{17}N_3O_2S$, monoclinic, $P2_1/n$ (no. 14), $a = 9.0650(15)$ Å, $b = 16.342(3)$ Å, $c = 10.1187(17)$ Å, $\beta = 91.061(5)$ Å. $V = 1498.7(4)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0645$, $wR_{ref}(F^2) = 0.1323$, $T = 308$ K.

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The title crystal structure is shown in the figure. Table 1 contains details on crystal structure and measurement conditions. Table 2 lists the atoms with their coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.46 × 0.35 × 0.11 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	2.2 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX, ω
$2\theta_{max}$, completeness:	56.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	38065, 3694, 0.171
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1880
$N(param)_{refined}$:	191
Programs:	Bruker [1], SHELX [2], PLATON [3]

Source of materials

The title compound was synthesized from the Sonogashira Coupling-Aminovinylation Sequence reaction [4]. In a nitrogen atmosphere, a THF solution of phenylacetylene (1.1 mmol in 5 mL THF) was added dropwisely into a stirred mixture of 2-bromo-5-nitrothiazole (1 mmol), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol), CuI (7 mg, 0.04 mmol), and 11 mL of THF/NEt_3 (10:1). The reaction mixture was stirred at room temperature overnight until conversion was complete (monitored by TLC). Then, a solution of diethylamine (2 mmol) in 5 mL of methanol was added, and the mixture was heated to reflux for *ca*. 9 hour until complete conversion (monitored by TLC). The solvents were evaporated *in vacuo*, and the residue was purified by chromatography over a short pad of aluminum oxide eluting with dichloromethane followed by acetone to yield 60% of the entitled compound. The residue was then recrystallized in dichloromethane by evaporation *in vacuo*, which yielded dark red crystals. After several attempts a suitable crystal for single X-ray diffraction study was obtained.

Experimental details

H atoms were fixed geometrically at ideal positions and allowed to ride on the parent atoms with C–H = 0.93–0.97 Å, with $U_{iso}(H) = 1.5U_{eq}(C)$ (for CH_3)and 1.2 $U_{eq}(C)$ (for CH_2 and CH).

***Corresponding author: Noor Aisyah Ahmad Shah,** Department of Chemistry and Biology, Center for Defence Foundation Studies, Universiti Pertahanan Nasional Malaysia, Kem Sungai Besi, 57000 Kuala Lumpur, Malaysia, e-mail: aisyah@upnm.edu.my
Nur Farahin Pairan and Noor Azilah Mohd Kasim: Department of Defence Science, Faculty of Science and Technology Defence, Universiti Pertahanan Nasional Malaysia, Kem Sungai Besi, 57000 Kuala Lumpur, Malaysia
Bohari M. Yamin: School of Chemical Sciences and Food Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
S1	0.26201(8)	0.10068(4)	0.47756(7)	0.0470(2)
O1	0.4724(2)	0.07587(15)	0.1519(2)	0.0784(7)
O2	0.5499(2)	0.08282(16)	0.3544(2)	0.0826(8)
N1	0.4499(3)	0.08231(15)	0.2708(3)	0.0557(7)
N2	0.0524(2)	0.09474(14)	0.3003(2)	0.0481(6)
N3	−0.1649(2)	0.13767(13)	0.7209(2)	0.0449(6)
C1	0.1802(3)	0.08721(16)	0.2366(3)	0.0501(7)
H1A	0.1837	0.0811	0.1453	0.060*
C2	0.3035(3)	0.08905(16)	0.3135(3)	0.0425(7)
C3	0.0761(3)	0.10336(14)	0.4305(2)	0.0374(6)
C4	−0.0452(3)	0.11319(15)	0.5152(3)	0.0417(6)
H4A	−0.1383	0.1069	0.4762	0.050*
C5	−0.0423(3)	0.13083(15)	0.6478(3)	0.0388(6)
C6	0.1002(3)	0.14565(16)	0.7180(2)	0.0393(6)
C7	0.1627(3)	0.22314(17)	0.7157(3)	0.0482(7)
H7A	0.1157	0.2650	0.6691	0.058*
C8	0.2938(3)	0.2384(2)	0.7817(3)	0.0588(9)
H8A	0.3357	0.2903	0.7795	0.071*
C9	0.3625(3)	0.1766(3)	0.8507(3)	0.0641(10)
H9A	0.4499	0.1872	0.8971	0.077*
C10	0.3039(3)	0.0993(2)	0.8522(3)	0.0596(8)
H10A	0.3525	0.0576	0.8980	0.072*
C11	0.1722(3)	0.08324(18)	0.7855(3)	0.0481(7)
H11A	0.1323	0.0308	0.7861	0.058*
C12	−0.1625(3)	0.16785(18)	0.8579(3)	0.0545(8)
H12A	−0.2408	0.2077	0.8679	0.065*
H12B	−0.0694	0.1954	0.8754	0.065*
C13	−0.1815(4)	0.1006(2)	0.9588(3)	0.0812(11)
H13A	−0.1791	0.1237	1.0460	0.122*
H13B	−0.1031	0.0615	0.9509	0.122*
H13C	−0.2746	0.0738	0.9435	0.122*
C14	−0.3122(3)	0.12774(17)	0.6616(3)	0.0475(7)
H14A	−0.3792	0.1086	0.7286	0.057*
H14B	−0.3086	0.0865	0.5929	0.057*
C15	−0.3710(3)	0.20648(18)	0.6031(3)	0.0585(8)
H15A	−0.4676	0.1972	0.5654	0.088*
H15B	−0.3061	0.2251	0.5354	0.088*
H15C	−0.3767	0.2472	0.6711	0.088*

Comment

Thiazole derivatives are important heterocyclic compounds for biological and pharmaceutical activities. The role of the thiazole is already exhibited by most epotilones used against multi-drug resistant tumor [5] and treatment of type 2 diabetes [6]. Organic non-linear optics (NLO) materials formed by a donor-acceptor pair in their molecular system exhibit noteworthy NLO characteristics [7]. Thiazoles with a push-pull system containing electron-withdrawing and electron donating groups have been studied in the past years in order to develop derivatives to be used as NLO materials [7, 8]. On the other hand, it is well known as an excellent ligand [9, 10].

The title compound consists of a nitrothiazole and a benzyldiethylamine group connected by the C4–C5 double bond. It adopts the *E* configuration. The whole molecule is not planar. However, the nitrothiazole S1/O1/O2/N1/N2/(C1–C4) fragment is almost planar with maximum deviation of 0.029(2) Å for O1 from the least-squares plane. This plane and the plane of the phenyl moiety enclose an angle of 82.57(10)°. The double bond C4—C5 has a length of 1.372(3) Å. Distances C2—S1 and C3—S1 are 1.719(3) Å and 1.743(3) Å respectively, showing a partial double bond character for the bonds compared to 1.714(2) and 1.713(2) Å in 2-bromo-4-phenyl-1,3-thiozole [11]. The N2—C3 bond distance of 1.338(3)° is longer than that of the analoguous one (1.295(2) Å) indicating a degree of delocalisation due to the conjugation effect. Other bond lengths and angles are in normal ranges.

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