

A Novel Synthesis and Crystal Structure of 3,5-Substituted-3H-[1,3,4]thiadiazole-2-thione

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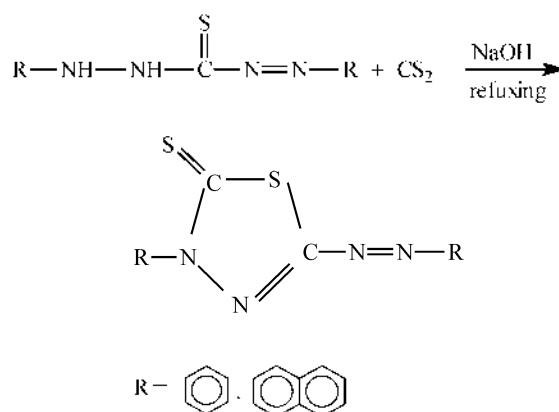
Key Words : Synthesis, Crystal structure, 3H-[1,3,4]Thiadiazole-2-thione derivation

Thiadiazole and its derivations are important organic reaction intermediates and they have been widely used as insecticides, fungicides and agricultural pesticides. Generally, synthesis of the thiadiazole derivations needs high temperature ($\geq 100^\circ\text{C}$) or low temperature ($< 0^\circ\text{C}$) or high pressure (at least higher than 1 atmospheric pressure), and the yields of those reactions are low.¹ Otherwise, they could be synthesized by reacting thiocarbonyl dichloride with dithizone.² However, in our laboratory, when we investigated reaction of dithizone with carbon bisulfide and sodium hydroxide solution under very mild conditions, we obtained the 3-phenyl-5-phenylazo-3H-[1,3,4]thiadiazole-2-thione (compound **1**) in high yield and we were also able to obtain the single crystal. In order to study the reproducibility of this novel reaction, we adopted the same method and chose di- α -naphthylthiocarbazono to react with carbon bisulfide and sodium hydroxide solution. As expected, 3-naphthyl-5-naphthylazo-3H-[1,3,4] thiadiazole-2-thione (compound **2**) as a single crystal was obtained. This paper is to describe the synthesis and the molecular structures of these two compounds.

Experimental Section

All chemicals were obtained from a commercial source and used without additional purification. Di- α -naphthylthiocarbazono was prepared according to the literature method.³

Synthesis: Dithizone (2 g, 8.0 mmol) was dissolved in acetonitrile (80 ml.). To this solution was added the mixture of carbon bisulfide (16.0 mmol) and 50% aqueous sodium hydroxide (8.0 mmol) with stirring at 40°C . The reaction mixture was kept at 40°C for 4 h, and the red precipitate was formed, then it is cooled to room temperature. The products of compound **1** were collected and the red crystals were obtained by recrystallization from EtOH. Yield 86%, mp $178\text{--}180^\circ\text{C}$. Calc. for $\text{C}_{14}\text{H}_{10}\text{N}_4\text{S}_2$: C, 56.30; H, 3.37; N, 18.78%. Found: C, 53.04; H, 3.11; N, 18.06%. IR (KBr), ν_{max} : 3060 ($\text{C}_{\text{Ar}}\text{--H}$), 1587, 1515, 1487, 1457 ($\text{C}_{\text{Ar}}\text{--C}_{\text{Ar}}$); 1314 ($\text{C}=\text{S}$); 680 ($\text{C}\text{--S}$); 1246 ($\text{C}_{\text{Ar}}\text{--N}$) cm^{-1} .^{4,5} Compound **2** was prepared with the same procedure as described for the compound **1** except that di- α -naphthyl-thiocarbazono (2.8 g,



Scheme 1. Synthesis pathway of the title compounds.

8.0 mmol) was used to replace the dithizone. Yield 82%, mp $206\text{--}207^\circ\text{C}$. Calc. for $\text{C}_{22}\text{H}_{14}\text{N}_4\text{S}_2$: C, 66.30; H, 3.54; N, 14.06. Found: C, 66.18; H, 3.48; N, 14.01. IR (KBr), ν_{max} : 3054 ($\text{C}_{\text{Ar}}\text{--H}$), 1627, 1600, 1545, 1510 ($\text{C}_{\text{Ar}}\text{--C}_{\text{Ar}}$); 1340 ($\text{C}=\text{S}$); 773 ($\text{C}\text{--S}$); 1251 ($\text{C}_{\text{Ar}}\text{--N}$) cm^{-1} .^{4,5}

The synthesis pathway of the title compounds is shown in the Scheme 1.

X-Ray structures of the title compounds: The selected crystals of the compounds **1** and **2** were mounted on a glass fiber. The data were collected with graphite monochromated Mo- $\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation at the temperature 293 K . Both of the collected data were reduced by using the program *SAINTE*⁶ and empirical absorption correction was done by using the *SADABS*⁷ program. The structures were solved by direct method and refined by full-matrix least-squares method on F_{obs}^2 by using the *SHELXTL*⁸ software package. All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined geometrically. For **1**, final conventional $R_1 = 0.0858$, $wR_2 = 0.1471$, $S = 1.201$; and for **2**, the corresponding $R_1 = 0.1125$ and $wR_2 = 0.2861$, $S = 1.029$.

Results and Discussion

Compound **1** crystallizes in the monoclinic system, space group $C/2c$ with $a = 25.310(5)$, $b = 3.9763(8)$, $c = 30.244(6)$ \AA , $\beta = 113.86(3)^\circ$, $\text{C}_{112}\text{H}_{80}\text{N}_{32}\text{S}_{16}$, $M_r = 2387.04$, $V = 2783.6$

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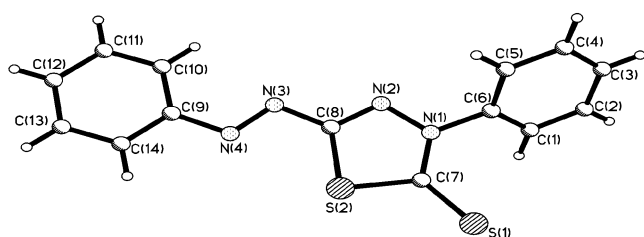


Figure 1. Molecular structure with the atomic numbering scheme for compound **1**.

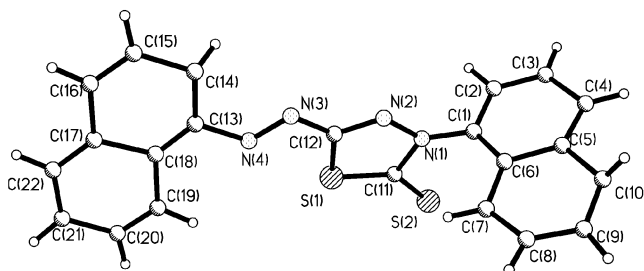


Figure 2. Molecular structure with the atomic numbering scheme for compound **2**.

(10) Å³, $Z = 1$, $D_c = 1.424$ g/cm³, $F(000) = 1232$, $\mu = 0.376$ mm⁻¹, and **2** crystallizes in the triclinic, $P\bar{1}$, $a = 7.4078(15)$, $b = 10.896(2)$, $c = 12.226(2)$ Å, $\alpha = 94.22(3)^\circ$, $\beta = 90.31(3)^\circ$, $\gamma = 103.32(3)^\circ$, $C_{22}H_{14}N_4S_2$, $M_r = 398.49$, $V = 957.3(3)$ Å³, $Z = 2$, $D_c = 1.382$ g/cm³, $F(000) = 412$, $\mu = 0.293$ mm⁻¹, respectively. The displacement ellipsoid plot with the numbering scheme for **1** and **2** are shown in Figure 1 and Figure 2, respectively.

The crystal structures of the two compounds are very similar and consist of monomeric 3-phenyl-5-phenylazo-3H-[1,3,4]thiadiazole-2-thione and 3-naphthyl-5-naphthylazo-3H-[1,3,4]thiadiazole-2-thione, respectively. Bond lengths and angles in the phenyl ring and naphthyl ring are generally normal. In compound **1**, the bond lengths of N(3)-N(4) [1.262(5) Å], S(1)-C(7) [1.642(4) Å] and N(2)-C(8) [1.293(5) Å] are all slightly longer than typical double-bond values of

N=N [1.25 Å], S=C [1.62 Å] and N=C [1.27 Å],⁹ respectively, indicating that these bonds have double-bond character. This phenomenon is also found in compound **2**. The double bond lengths of S(1) = C(7) [1.642(4) Å] in **1** and S(2) = C(11) [1.690 Å] in **2** are all shorter than that of reported in dithizone [1.692(4) Å].¹⁰ In two compounds, eight atoms of the five-member thiadiazole ring, 5-substituted sulfur atom and two nitrogen atoms of azo-group are almost lie in a plane, with largest deviation 0.054 Å for these two compounds.

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Supporting Information Materials. Listing of atomic coordinates, complete bond distances and angles, thermal parameters, and least-squares results for the title compounds are available on request from the corresponding author.

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