A Novel Synthesis and Crystal Structure of 2,3-Substituted-1,4-2H-tetrazolthione

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The tetrazole derivatives have been extensively studied due to their explosive properties and biological importances in agriculture, biochemistry and pharmacology.[1] Tetrazolthiones show antibacterial activity and they are known as good weed killers.[2] In general, tetrazolthione derivatives were synthesized by the reactions of alkyl isothiocyanates with azides, or by the reactions of alkyl isoaminothiourea with nitrous acid. However, only 1,4-substituted tetrazolthiones could be prepared in these methods.[3] In our laboratory, we found a new ring-closing reaction of dithizone with carbon disulfide to afford 2,3-disubstituted tetrazolthiones in high yields. By this method, 2,3-diphenyl-1,4-2H-tetrazolthione (**1**) and 2,3-di(*p*-methyl-phenyl)-1,4-2H-tetrazolthione (**2**) were synthesized and characterized by X-ray crystallography. In this paper, we describe the synthesis of the two compounds and the crystal structure of **2**.

Experimental Section

All chemicals were obtained from a commercial source and used without additional purification.

Synthesis. Dithizone (2.0 g, 8.0 mmol) was dissolved in acetonitrile (80 mL). To this solution was added the mixture of carbon disulfide (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 to form red precipitates, and then it is cooled to room temperature. The red crystalline solids were collected by filtration and recrystallize from EtOH to give **1**. Yield: 86%, mp 167-168 °C. Calc. for $C_{13}H_{12}N_4S$: C, 60.91; H, 4.71; N, 21.86%. Found: C, 60.85; H, 4.67; N, 21.79%. IR (KBr), ν_{max}: 3440 (N-H), 3010 (C_{Ar}-H), 1588, 1487, 1463 (C_{Ar}-C_{Ar}), 1315 (C=S), 1244 (N-N, C_{Ar}-N),[4,5] 979, 763 (C_{Ar}-H) cm^{-1}.

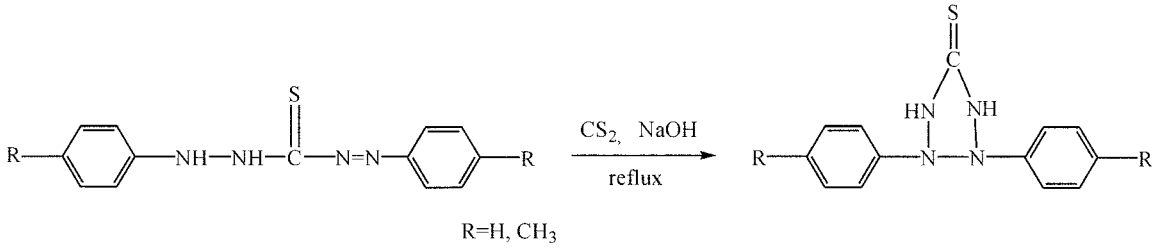
Compound **2** was prepared with the same procedure as described for **1** except that *p,p'*-dimethyl-dithizone (2.3 g, 8.0 mmol) was used to replaced the dithizone. Yield 90%, mp 169-171 °C. Calc. for $C_{15}H_{16}N_4S$: C, 63.29; H, 5.67; N, 19.71%. Found: C, 63.20; H, 5.70; N, 19.64%. IR (KBr), ν_{max}: 3432 (N-H), 3027 (C_{Ar}-H), 2990, 2920 (C_{methyl}-H), 1506, 1401 (C_{Ar}-C_{Ar}), 1296 (C=S), 1241 (N-N,C_{Ar}-N),[5,6] 980, 826, 712 (C_{Ar}-H) cm^{-1}.

The synthetic pathway is shown in Scheme 1.

X-ray Structures of 2. The selected crystals of **2** were mounted on a glass fiber. The data were collected with graphic monochromated Mo-Kα (λ = 0.71073 Å) radiation at 293 K. The collected data were reduced by using the program *SAINT* and the empirical absorption correction was done by using the *SADABS* program. The structure was solved by direct method and refined by full-matrix least-squares method on F_{obs}^2 by using the *SHELXTL* program. All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined geometrically. Final conventional R_1 = 0.1089, wR_2 = 0.3064, S = 1.219.

Results and Discussion

Compound **2** was crystallized in the orthorhombic system, space group $Pmn2_1$ with a = 18.381 (4), b = 6.180 (1), 6.187(1) Å, $C_{15}H_{16}N_4S$, M_r = 284.38, V = 702.7 (2) Å^3, Z = 2, D_c = 1.344 g/cm^3, F (000) = 300, μ = 0.226 mm^{-1}. The OPTEP drawing with the numbering scheme for **2** is shown in Figure 1.



Scheme 1

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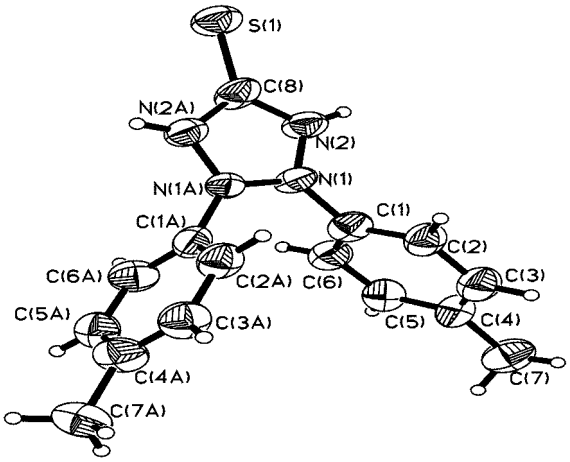

Figure 1. Molecular structure with the atomic numbering scheme for **2**.

The crystal structure consists of two 2,3-di(*p*-methylphenyl)-1,4-2H-tetrazolthione molecules. The bond lengths and angles in the phenyl ring are generally normal. The N(1) atom, C(7) atom and phenyl ring fall within a plane. The plane equation is $14.6972x + 2.6120y - 2.6395z = 0.7440$, with the largest atom deviation is 0.019 Å The bond lengths and angles in the tetrazole ring are comparable to those reported before.[6,7] The N(1)-N(2) bond distance, 1.313(8) Å, is indicative of some double-bond character. The least-squares planes of phenyl ring and tetrazole ring are almost perpendicular, with the dihedral angle being 89.65°. The bond length of S(1)-C(8), 1.686 (10) Å, is in the normal range.

In the crystal lattice, there exists a C-H$\cdots\pi$ supramolecule interaction.[8,9] The distance between C(7)-H(7A) to phenyl ring is 3.030 Å, which stabilizes the crystal structure.

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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 **1** and **2** are available on request from the corresponding author.

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