

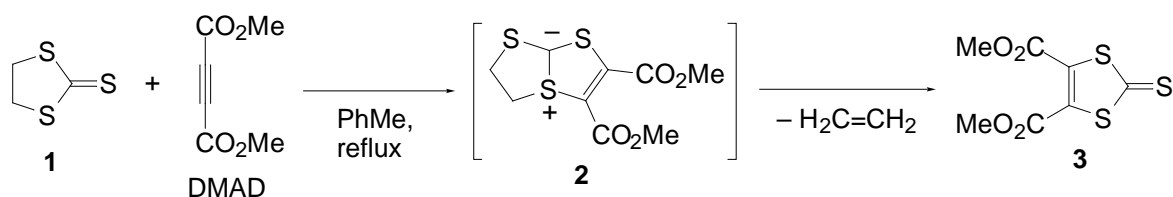
REACTIONS OF 1,3-DITHIOLANE-2-THIONE AND 1,3-DITHIOLE-2-THIONES WITH 4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE (PTAD)

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Abstract - 1,3-Dithiolane-2-thione (**1**) and 1,3-dithiole-2-thione (**18a**) reacted with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) to provide betaines, 4-phenyl-1-[2-(1,3-dithiolanio)]urazolide (**8**) (79%) and 4-phenyl-1-[2-(1,3-dithiolio)]-urazolide (**19a**) (73%), respectively. A mechanism, involving three-membered ring formation by an electrophilic 1,2-addition of the PTAD nitrogen atom to the C=S bond, is proposed. Discussion on the structure of **8** is made in some detail based on the spectroscopic data and X-Ray crystallographic analysis.

It is well documented that 1,3-dithiolane-2-thione (**1**) reacts with dimethyl acetylenedicarboxylate (DMAD) to furnish 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione (**3**) in a satisfactory yield.¹ This synthetically useful reaction, a key step for the preparation of tetrathiafulvalene (TTF), has been believed to take place through a 1,3-dipolar cycloaddition that yields an ylide intermediate (**2**), which undergoes a retro-1,3-dipolar cycloaddition to produce **3** and ethylene.

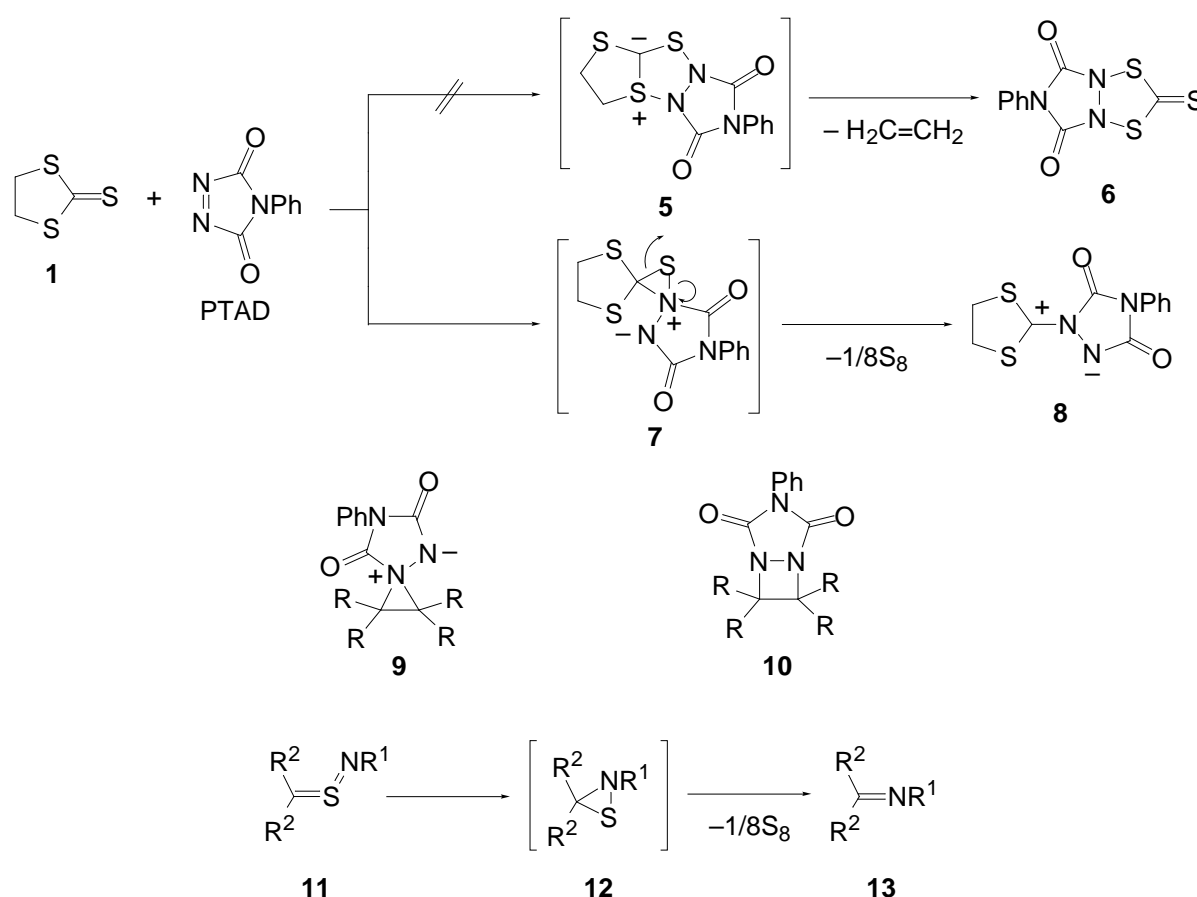


For several years we have been investigating reactions of 1,3-dithiolane-2-thione and the related compounds with 1,3-dipolarophiles.² In the extension of these studies, we have turned our attention to the reaction of **1** with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD). In analogy with the reaction of **1** with DMAD, we expected the formation of compound (**6**), which possesses a new heterocyclic ring system, through intermediary formation of a 1,3-dipolar cycloadduct (**5**). Interestingly, however, the reaction resulted in the formation of a betaine, 4-phenyl-1-[2-(1,3-dithiolanio)]urazolide (**8**), and not the expected **6**.

The present paper reports that this type of reaction is quite general, thus **1** and the related compounds providing a series of the corresponding betaines on reactions with PTAD.

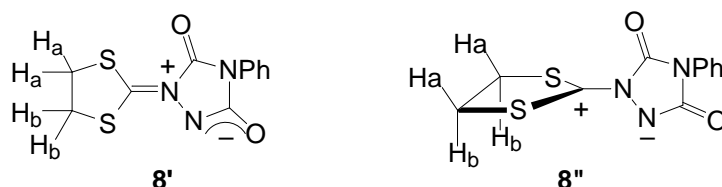
A 1:1 mixture of **1** and PTAD in CH₂Cl₂ was stirred at room temperature overnight, during which the original red mixture turned yellow. The resulting crystalline solid was collected by filtration. The crude product was washed with CS₂ to remove the elemental sulfur, formed by the reaction, thus providing 4-phenyl-1-[2-(1,3-dithiolanio)]urazolide (**8**) in 79% yield. Crystallization of the above product from CH₃CN twice afforded yellow needles of **8** suitable for X-Ray diffraction analysis.

The reaction probably involves the initial formation of a three-membered ring intermediate **7** by electrophilic addition of PTAD to **1**. It was reported that reactions of alkenes to PTAD, leading to [2+2] cycloadducts **10** as the final product, involves the initial formation of three-membered ring intermediates **9**, which correspond to **7**.³ Extrusion of a sulfur atom from **7** would produce **8** as the final product. A striking analogy of the sulfur extrusion from **7** is found in the sulfur extrusion of thione *S*-imides (**11**), which affords imines (**13**) through three-membered intermediates **12**.⁴

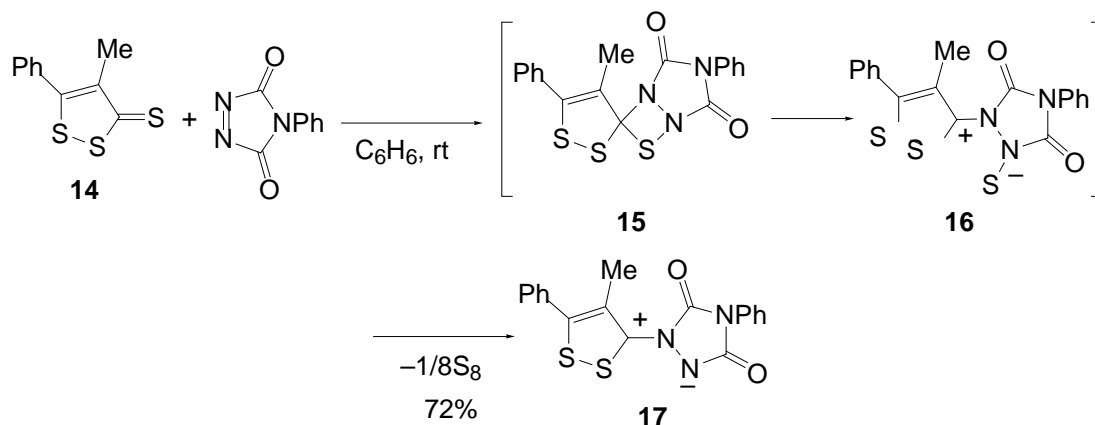


The two methylenes of **8** are magnetically non-equivalent, that is, their signals appeared as two multiplets at δ 3.82–3.88 and 4.01–4.07 in equal intensity in the ¹H NMR spectrum. This suggests that the free rotation about the pinch bond (C–N bond) is frozen at room temperature due to the contribution of the canonical structure (**8'**), thus making methylene protons H_a and H_b chemically non-equivalent. The methylene

protons would also appear as a set of multiplet, when the conformation of **8** is fixed to the conformer (**8'**) where the dithiolane and urazole rings are perpendicular to each other. This is not the case, however, because the ^{13}C NMR spectrum of **8** showed nine carbon peaks, two of which at δ 37.1, 41.9 originate from non-equivalent methylene carbons.

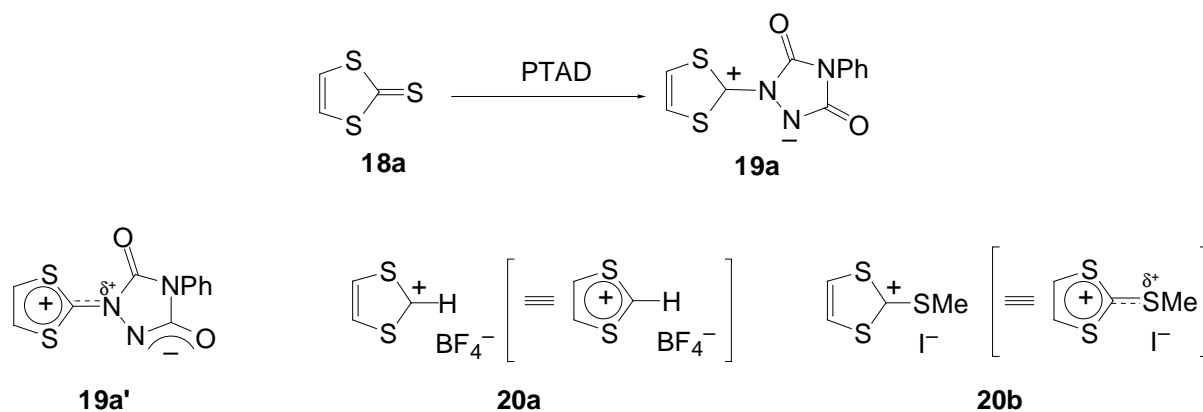


A literature survey revealed that a marked analogy to the present reaction is found in the reaction of a 1,2-dithiole-3-thione (**14**) with PTAD, which afforded a betaine (**17**).⁵ The authors proposed a mechanism involving a [2+2] cycloadduct (**15**) as an intermediate, which undergoes the C-S bond cleavage to give **17** by elimination of sulfur atom from **16**. We cannot rule out a possibility that the same mechanism is operative in our reaction.

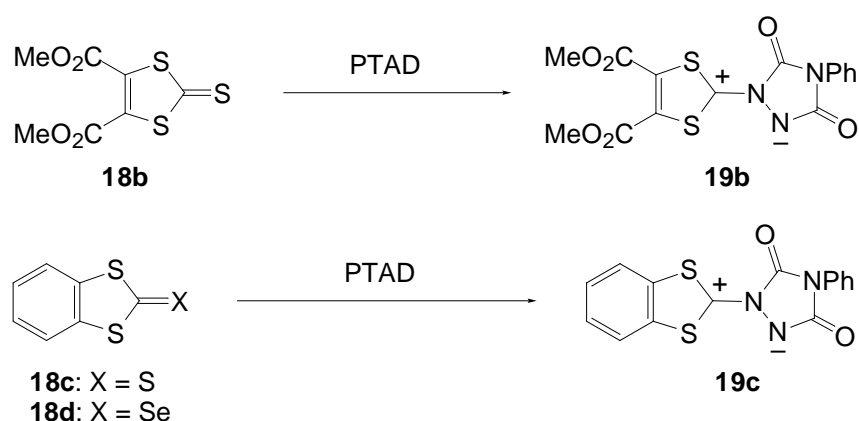


The reaction of 1,3-dithiole-2-thione (**18a**) with PTAD took place more rapidly to give 4-phenyl-1-[2-(1,3-dithiolio)]urazolid (**19a**) in 73% yield. Also in **19a**, the rotation about the pinch bond (C-N bond) is frozen at room temperature. In the ^1H NMR spectrum, the two hydrogen atoms of the dithiole ring appeared as a triplet-like multiplet centered at δ 7.85 because of the very close chemical shift values. A ^1H - ^1H COSY experiment revealed that the above multiplet is composed of two doublets both with $J = 6.8$ Hz. The ^{13}C NMR spectrum of **19a** showed nine peaks, thus revealing that the two vinylic carbons of the dithiole ring are magnetically non-equivalent. The carbon atom at the 2-position of the 1,3-dithiole ring in **19a** appears at δ 168.2. This chemical shift value is comparable with that of the corresponding carbon atom peak of the 1,3-dithiolium salt (**20b**), δ 166.4.⁶ The corresponding carbon atom of the parent 1,3-dithiolium salt (**20a**) resonates at a much lower field, δ 179.5.⁶ It is well documented that 1,3-dithiolium ions, which possess 6π -electrons, are aromatic.^{6,7} Taking these all into account, the structure

of **19a** would best be expressed by the canonical structure (**19a'**), where the positive charge is delocalized over the dithiole ring, in addition to over the nitrogen atom of the pinch bond, and the negative charge is delocalized over the N-C-O unit.



The reaction is general for 1,3-dithiole-2-thiones. Thus, 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione (**18b**) reacted with PTAD, though in a sluggish way compared with **18a**, to give 4-phenyl-1-{2-[4,5-bis(methoxycarbonyl)-1,3-dithiolio]}urazolide (**19b**) in 28% yield. Also in **19b**, the two CO₂Me groups are non-equivalent both in ¹H and ¹³C NMR spectra. 1,3-Benzodithiole-2-thione (**18c**) reacted with PTAD to provide a 73% yield of 4-phenyl-1-[2-(1,3-benzodithiolio)]urazolide (**19c**), which is hardly soluble in common organic solvents. 1,3-Benzodithiole-3-selone (**18d**) reacted with PTAD much rapidly than did **18c**; the reaction resulted in the immediate precipitation of metallic gray selenium from the reaction mixture to give a 78% yield of the same betaine (**19c**) as that obtained from **18c** and PTAD.



The variable temperature ¹H NMR spectra of **8** were measured with DMSO-d₆ as the solvent in order to determine the internal rotation barrier about the pinch bond. These experiments revealed that the rotation is still frozen even at 130 °C, that is, the multiplet pattern due to the methylene hydrogens of **8** was retained even at that temperature. It is therefore concluded that the pinch bond has a strong double bond character because of the contribution of the canonical structure (**8'**). Incidentally, **8** began to decompose at 100 °C and

decomposed nearly completely at 135 °C in DMSO- d_6 , which made it impossible to determine the spectra at higher temperatures than 130 °C.

Molecular structures of **8** are shown in Figure 1 along with the relevant bond lengths and bond angles data. The molecular structure of **8** is in good agreement with that predicted from the NMR data. The side view structure of **8** clearly shows that S₁, C₁₄, S₂, and the urazole ring atoms are placed on the same plane, thus indicating that strong conjugative interactions, which are best expressed by the canonical structure (**8'**), exist between the dithiolane and urazole rings. The C₁₄-N₅ bond length 1.34 Å is slightly shorter than the common C(sp²)-N(sp³) single bond length 1.36 Å and is longer than the common C-N double bond length 1.28 Å.⁸ The C₁₆-O₃ bond length 1.23 Å is longer than the C₉-O₄ bond length 1.19 Å in accordance with the contribution of the canonical structure (**8'**).

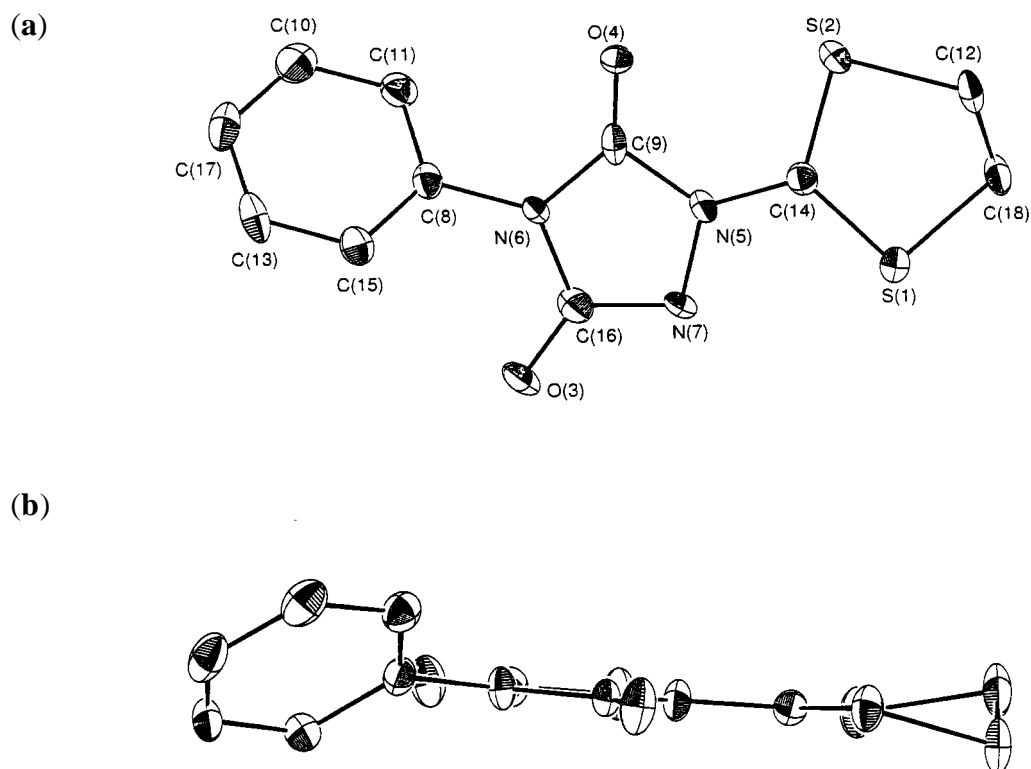


Figure 1. Molecular structures of **8**: (a) top view and (b) side view. Bond length data (Å): C14-S1, 1.6975(6); C14-S2, 1.7214(6); C14-N5, 1.3412(7); N5-C9, 1.4471(8); N5-N7, 1.4103(6); N7-C16, 1.3635(7); C9-O4, 1.1863(7); C16-O3, 1.2272(7). Bond angle data (°): C14-S1-C18, 94.4(1); C14-S2-C12, 91.9(1); S1-C14-S2, 120.4(1); S1-C14-N5, 118.5(1); S2-C14-N5, 121.1(1); N7-N5-C14, 118.8(1); C9-N5-C14, 126.4(1); N7-N5-C9, 114.9(1); N5-N7-C16, 102.4(1); N7-C16-N6, 110.8(1); N5-C9-N6, 100.8(1); N6-C16-O3, 125.2(1); N7-C16-O3, 124.0(1); N5-C9-O4, 125.4(1); N6-C9-O4, 133.7(1).

EXPERIMENTAL

Solvents were purified and dried in the usual manner. All the reactions were carried out under argon. Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX400, a Bruker AM400, or a Bruker AC200 spectrometer with TMS as the internal standard. IR and UV/Vis spectra were recorded on a Hitachi 270-50 and a JASCO V-560 spectrophotometer, respectively. Elemental analyses were performed by the Chemical Analysis Center of Saitama University. 1,3-Dithiolane-2-thione (**1**) and 1,3-dithiole-2-thione (**18a**) were used as purchased. 1,3-Dithioles (**18b**)¹ and (**18c,d**)⁹ were prepared according to the literature methods.

4-Phenyl-1-[2-(1,3-dithiolanio)]urazolide (**8**).

A solution of 412 mg (2.4 mmol) of PTAD in 25 mL of CH_2Cl_2 was added to a solution of 316 mg (2.4 mmol) of 1,3-dithiolane-2-thione (**1**) in 25 mL of the same solvent over a period of 10 min. The mixture was stirred overnight, during which the original red mixture turned a yellow suspension. The resulting crystalline precipitate was collected by filtration and washed with a small amount of CS_2 to remove the elemental sulfur, formed by the reaction, to give 393 mg (60%) of **8**. The filtrate was evaporated to give the solid residue, which was washed with small amounts of CH_2Cl_2 and then with CS_2 to give 125 mg (19%) of a second crop of **8**; combined yield, 79%. Crystallization of **8** from MeCN twice gave yellow plates suitable for X-Ray crystallographic analysis, which melted at 210–220 °C, solidified at about 235 °C, and melted again at 240–250 °C to give a dark brown oil: ^1H NMR (400 MHz, DMSO-d_6) δ 3.82–3.88 (m, 2H, CH_2), 4.01–4.07 (m, 2H, CH_2), 7.40–7.45 (m, 1H, Ph), 7.47–7.55 (m, 4H, Ph); ^{13}C NMR (100.6 MHz, DMSO-d_6) δ 37.1 (methylene C), 41.9 (methylene C), 125.8 (phenyl), 127.7 (phenyl), 128.7 (phenyl), 132.2 (phenyl), 148.7 (C=O), 154.6 (C=O), 174.0 (pinch bond C); UV/VIS (MeCN) λ_{max} (ϵ) 287 (8860), 391 nm (11100); IR (KBr) 2972, 1772, 1762, 1684, 1494, 1376, 1280, 1270, 1148, 782, 766, 702, 630 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_9\text{N}_3\text{O}_2\text{S}_2$: C, 47.30; H, 3.25; N, 15.04. Found: C, 47.25; H, 3.19; N, 15.08.

4-Phenyl-1-[2-(1,3-dithiolio)]urazolide (**19a**).

A solution of 143 mg (0.8 mmol) of PTAD in 20 mL of CH_2Cl_2 was added to a solution of 108 mg (0.8 mmol) of 1,3-dithiole-2-thione (**18a**) in 20 mL of the same solvent over a period of 10 min. The red homogeneous mixture turned a yellow suspension during 20 min. After stirring for 4 h at rt, the mixture was worked up in a manner similar to that described above to give 163 mg (73%) of **19a**: mp 246–250 °C; fine yellow granules (from MeCN); ^1H NMR (400 MHz, DMSO-d_6) δ 7.38–7.44 (m, 1H, phenyl), 7.48–7.54 (m, 4H, phenyl), 7.84–7.87 (triplet-like m, 2H, vinylene: a ^1H - ^1H COSY experiment revealed that the triplet is composed of two doublets with $J = 6.8$ Hz); ^{13}C NMR (100.6 MHz, DMSO-d_6) δ 124.8 (vinylene C), 125.6 (phenyl), 127.6 (phenyl), 128.3 (vinylene C), 128.8 (phenyl), 132.5 (phenyl), 148.6 (C=O), 154.6 (C=O), 168.2 (pinch bond C); UV/VIS (MeCN) λ_{max} (ϵ) 291 (3180), 410 nm (13400); IR (KBr) 3040, 1750, 1690, 1546, 1496, 1456, 1388, 1272, 1172, 1158, 1086, 1058, 792, 762, 722, 714,

698, 686, 634 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_7\text{N}_3\text{O}_2\text{S}_2$: C, 47.64; H, 2.54; N, 15.15. Found: C, 47.48; H, 2.52; N, 15.08.

4-Phenyl-1-{2-[4,5-bis(methoxycarbonyl)-1,3-dithiolio]}urazolide (19b).

A solution of 105 mg (0.6 mmol) of PTAD in 20 mL of CH_2Cl_2 was added to a solution of 150 mg (0.6 mmol) of 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione (**18b**) in 20 mL of the same solvent over a period of 10 min. The mixture was stirred overnight at rt and evaporated. The resulting residue was crystallized from AcOEt to give 110 mg (28%) of **19b**; mp 184.0-185.5 $^\circ\text{C}$; fine yellow granules; ^1H NMR (400 MHz, CD_3CN) δ 3.93 (s, 3H, Me), 3.94 (s, 3H, Me), 7.41-7.46 (m, 1H, Ph), 7.50-7.56 (m, 4H, Ph); ^{13}C NMR (100.6 MHz) δ 54.49, 54.52, 125.8, 128.1, 129.1, 132.2, 132.5, 136.2, 148.8, 154.9, 158.5, 158.6, 159.3; UV/VIS (MeCN) λ_{max} (ϵ) 298 (4550), 412 nm (16400); IR (KBr) 2925, 1768, 1742, 1696, 1586, 1494, 1432, 1372, 1264, 1190, 1176, 1106, 1018, 788, 770, 690, 626 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}_6\text{S}_2$: C, 45.80; H, 2.82; N, 10.68. Found: C, 46.01; H, 2.70; N, 10.53.

4-Phenyl-1-[2-(1,3-benzodithiolio)]urazolide (19c). (a) From 1,3-Benzodithiole-2-thione (18c). To a solution of 369 mg (2 mmol) of **18c** in 30 mL of CH_2Cl_2 was added 358 mg (2 mmol) of PTAD in three portions. The mixture was allowed to stand at rt overnight. The resulting flake-like crystals were collected by filtration to give 473 mg (73%) of **19c**, which is hardly soluble in organic solvents. Although crystallization from hot DMSO gave **19c** as fine yellow granules, considerable decomposition took place during this operation. **19c**: mp > 240 $^\circ\text{C}$ (no distinct melting point with decomposition); ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ 7.37-7.47 (m, 1H), 7.48-7.60 (m, 4H), 7.62-7.74 (m, 2H), 8.23-8.37 (m, 2H); UV/VIS (MeCN) λ_{max} (ϵ) 296 (4280), 412 nm (13500); IR (KBr) 3084, 1724, 1532, 1500, 1440, 1398, 1260, 1156, 1080, 1056, 994, 790, 754, 714, 696, 630 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_9\text{N}_3\text{O}_2\text{S}_2$: C, 55.03; H, 2.77; N, 12.84. Found: C, 54.93; H, 2.71; N, 12.79.

(b) From 1,3-Benzodithiole-2-selone (18d). A solution of 140 mg (0.8 mmol) of PTAD in 20 mL of CH_2Cl_2 was added to a solution of 148 mg (0.8 mmol) of **18d** in 15 mL of the same solvent over a period of 10 min. Immediately after mixing of the reactants, **19c** and grey metallic selenium began to separate. The mixture was allowed to stand for 2 h, and the resulting mixture of **19c** and the metallic selenium were collected by filtration. The mixture was extracted by use of a Soxhlet extractor with MeCN (100 mL) as the solvent to remove the metallic selenium, which is insoluble in MeCN. The continuous extraction for 15 h furnished 128 mg (78%) of **19c**.

X-Ray Crystallographic Analysis of 8.

Single crystal **8** was mounted on a MAC Science DIP3000 diffractometer with a graphite-monochromator at -120°C . Oscillation and nonscreen Weissenberg photographs were collected on the imaging plates of the diffractometer by using $\text{Mo}-K_\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and the data collection was made by the Denzo for all observed reflections. The structure were solved by direct methods using SIR92 in the maXus program system. The atomic coordinates and the anisotropic thermal parameters of the non-H atoms were refined by full matrix least squares. Crystal data of **8**: chemical formula, $\text{C}_{11}\text{H}_9\text{N}_3\text{O}_2\text{S}_2$; formula weight,

279.340; crystal size, 0.40 x 0.14 x 0.08 mm; crystal system, orthorhombic; space group, unit-cell dimensions, $a = 10.1880(5)$, $b = 7.2060(3)$, $c = 31.945(2)$ Å; volume of unit cell, 2345.2(2) Å³; P_{bca} ; Z , 8; D_x , 1.582 Mg m⁻³; number of total reflections measured, 2749; number of observed reflections 1682 [$I > 2.00 \sigma(I)$]; number of parameters varied, 175; R , 0.077 [0.055 for $I > 2.00 \sigma(I)$]; R_w , 0.106; S , 1.967.

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