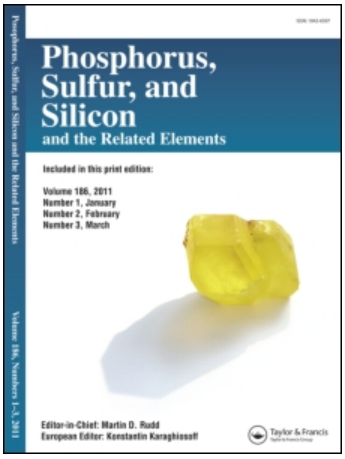

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REACTIONS OF A ZWITTERIONIC BENZYLIDENE COMPOUND OF THIOOXALIC ACID HYDRAZIDE AMIDE HYDRAZONE WITH C_1-BUILDING BLOCKS

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REACTIONS OF A ZWITTERIONIC BENZYLIDENE COMPOUND OF THIOOXALIC ACID HYDRAZIDE AMIDE HYDRAZONE WITH C_1-BUILDING BLOCKS

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The zwitterionic 4-methoxybenzylidene derivative of thiooxalic acid hydrazide amide hydrazone **1** reacts with orthocarboxylic esters to 2,5-disubstituted 1,3,4-thiadiazoles **2** and with carbon disulfide or 1,1'-carbonyldiimidazole to the corresponding 2,3-dihydro-1,3,4-thiadiazoles **4** and **5**. The acyclic zwitterionic products **3** were obtained from **1** with aromatic acyl chlorides. X-Ray structural data of **2a** and **2b** are given. All compounds are characterized by spectroscopic data (^{1}H NMR, ^{13}C NMR, IR).

Keywords: zwitterionic monobenzylidene thiooxalic acid hydrazide amide hydrazone; C_1-building blocks; 1,3,4-thiadiazoles; X-ray analysis; NMR data

INTRODUCTION

In the past we reported the synthesis of the zwitterionic thiooxalic acid 2-amide-1-hydrazide-2-hydrazone (oxalic acid thiohydrazide amide hydrazone)[1] and their characterization by X-ray analysis.[2] Later we described the reactions of this compound with aldehydes and ketones to the zwitterionic monobenzylidene thiooxalic acid hydrazide amide hydrazone **1** or substituted 2,3-dihydro-1,3,4-thiadiazoles, respectively.[3]

*Corresponding author.

In continuation of our work, the reaction of **1** with C_1-building blocks, e.g. orthocarboxylic esters, acyl chlorides, carbonyl disulfide or 1,1′-carbonyldiimidazole is reported in this work.

RESULTS AND DISCUSSION

The zwitterionic monobenzylidene thiooxalic acid hydrazide amide hydrazone **1** is a versatile starting material.

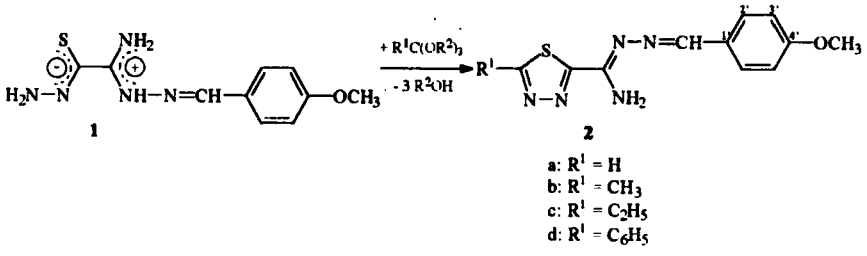
The reaction of **1** with different orthocarboxylic esters gives 5-alkyl(aryl)-1,3,4-thiadiazole-2-[2-(4-methoxybenzylidene)carboxamide hydrazones] **2a–d** in high yields (Scheme 1).

The ^1H and ^{13}C NMR spectra prove the 1,3,4-thiadiazole structure of compound **2**. In the ^1H NMR spectra, beside the signals for the aromatic protons and the CH=N proton, only one signal for the NH_2 group was found.

The exact assignment of the ^{13}C signals was confirmed by recording the COLOC and coupled (gated decoupling) ^{13}C NMR spectra. Thus, in the COLOC spectrum of **2b**, correlations were found, beside others, between S-C(R^1)=N/CH_3 and S-C=N/NH_2, respectively. In the coupled ^{13}C NMR spectrum of **2b** the S-C=N signal appears as triplet with the coupling constant ^3J(S-C=N, NH_2) ≈ 4.9 Hz, corresponding to the values found for the comparable 2,3-dihydro-1,3,4-thiadiazoles[3], whereas the carbon atom of the N=C-NH_2 group gives a singlet.

Additionally, the structural proof was furnished also by an X-ray crystal structure analysis of compounds **2a** and **2b** (for **2a** see Fig. 1).

It is known that 1,3,4-thiadiazoles can be synthesized from thiohydrazides and acylation agents.[4–6] In analogy, compound **1** reacts with acetyl chloride to yield also the 1,3,4-thiadiazole **2b** (cf. Scheme 2 and Method B).



SCHEME 1

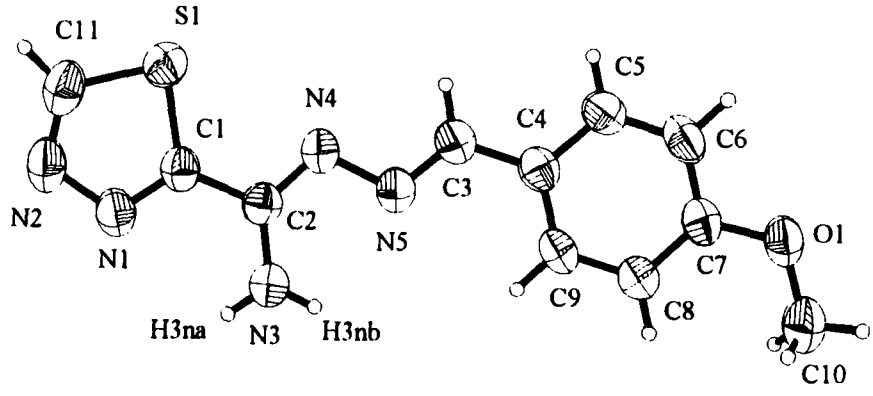
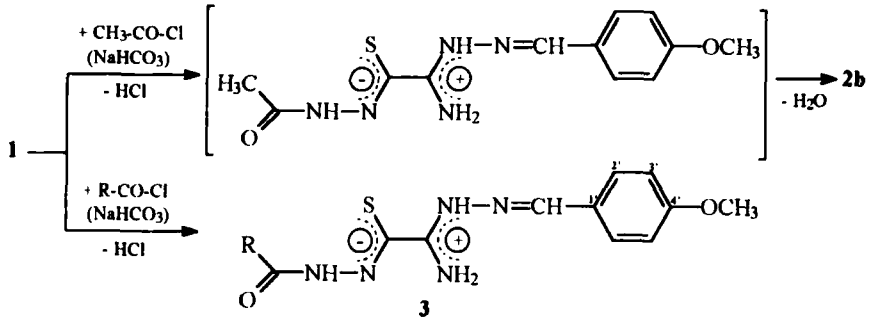


FIGURE 1. X-ray molecular structure of **2a**. Selected bond distances (Å) and angles (°). S1-C1 1.713(3), S1-C11 1.715(4), N1-N2 1.381(4), N1-C1 1.294(4), N2-C11 1.286(5), N4-N5 1.398(4), N4-C2 1.293(4), N5-C3 1.270(4), N3-C2 1.339(4), C1-C2 1.468(4), H3na···N1 2.499(11), H3nb···N5 2.342(8), C1-S1-C11 85.8(2), C1-N1-N2 112.2(3), C11-N2-N1 111.2(3), C2-N4-N5 111.4(3), C2-C1-S1 121.5(2), C3-N5-N4 113.9(3), N1-C1-S1 115.0(2), N2-C11-S1 115.9(3), N1-C1-C2 124.0(3), N4-C2-C1 115.9(3), N4-C2-N3 126.7(3), N5-C3-C4 122.8(3), N3-C2-C1 117.4(3).

In comparison with that fact aromatic acyl chlorides react with **1** to the zwitterionic thiooxalic acid 2-amide-1-(2-benzoylhydrazide)-2-[2-(4-methoxybenzylidene)hydrazones] **3a–d**. The aromatic residue stabilizes the acyclic zwitterionic structure contrary to the methyl group (Scheme 2). The structure of **3** is in accordance with the ^{1}H and ^{13}C NMR spectra. Four signals were found for the NH and NH_2 protons, two of which, in the range of 9.00–9.40 ppm, can be assigned to the NH_2 group corresponding to the NH_2 signals of the zwitterionic structure **1**.[3]



a: R = C_6H_5
b: R = 4-CH_3-C_6H_4
c: R = 4-Br-C_6H_4
d: R = 4-Cl-C_6H_4

SCHEME 2

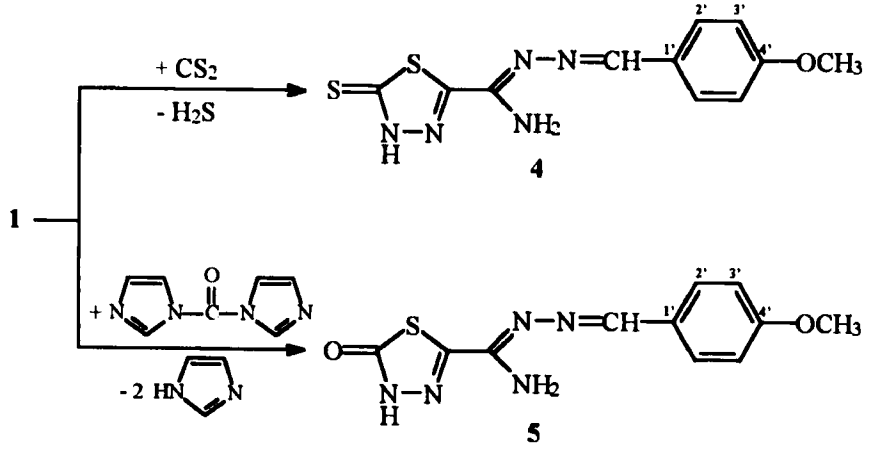
Furthermore, carbon disulfide is a reactive C_1-building block to prepare derivatives of 1,3,4-thiadiazoles with thiohydrazides.[7–10] Reaction of **1** with CS_2 gives the 2,3-dihydro-2-thiono-1,3,4-thiadiazole-5-[2-(4-methoxybenzylidene)-carboxamide hydrazone] **4** (Scheme 3).

1,1′-Carbonyldiimidazole is a versatile agent that transfers the acyl residue to amino groups of amino acids and peptides.[11] The reaction of **1** with carbonyldiimidazole in 1,2-dimethoxyethane affords the 2,3-dihydro-2-oxo-5-[2-(4-methoxybenzylidene)carboxamide hydrazone] **5** which was separated in good yield (Scheme 3). The structures of **4** and **5** were established by the analytical and spectral data. The ^{13}C NMR spectrum of **4** reveals the signal for the C=S group at δ = 189.4 and in case of **5** the signal for the carbonyl group at δ = 171.9. In the ^1H NMR spectra of **4** and **5** the signals for NH_2 and NH appear in the expected range. Additionally the IR spectrum of **5** showed the presence of one amide C=O group stretching at 1655 cm^{-1}.

In analogy to **2**, the assignments of the C atoms of S-C=N and N=C-NH_2 for **3–5** were done on the basis of the coupled ^{13}C NMR spectra, in which singlets were found for the N=C-NH_2 group, whereas the S-C=N carbon gives a broad multiplet due to the coupling about three bonds with the NH_2 and NH protons in each case.

EXPERIMENTAL

Melting points were determined with a Boëtius micro heating stage (Carl Zeiss Jena) without correction. Elementary analyses were performed by a CHNS-932



SCHEME 3

LECO analyzer. IR spectra (KBr) were recorded on a 205 FT-IR spectrophotometer. Mass spectra were taken on an AMD 402-3 spectrometer (Intectra GmbH). The ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker spectrometers AC 250 and ARX 300. The calibration of the spectra was carried out by means of solvent peaks (DMSO-d_6: δ^1H = 2.50; δ^{13}C = 39.7).

5-Alkyl(aryl)-1,3,4-thiadiazole-2-[2-(4-methoxybenzylidene)carboxamide hydrazones] *2a–d*

General Procedure

Method A: A solution of corresponding orthocarboxylic esters (2 mmol) in dry 1,2-dimethoxyethane (10 ml) is added dropwise to a stirred solution of **1** (2 mmol) in dry 1,2-dimethoxyethane (40 ml). The reaction mixture is refluxed for 2 h. Then the mixture is cooled and the resulting orange precipitate filtered off. Compounds **2a–d** are crystallized from ethanol.

2a: Yield 65%, mp 166–167 °C, orange needles. ^{1}H NMR (DMSO-d_6): δ(ppm) 3.79 (s, 3H, OCH_3); 7.00 (m, 2H, C_6H_4-3′); 7.31 (s, 2H, NH_2); 7.89 (m, 2H, C_6H_4-2′); 8.39 (s, 1H, CH=N); 9.65 (s, 1H, S-CH=N). ^{13}C NMR (DMSO-d_6): δ(ppm) 55.5 (OCH_3); 114.3 (C_6H_4-3′); 127.7 (C_6H_4-1′); 130.1 (C_6H_4-2′); 151.4 (N-C=N); 155.7 (CH=N); 156.0 (S-C=N); 161.4 (C_6H_4-4′); 164.9 (S-CH=N). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3480, 3387, 3336 (NH_2); 1615, 1605, 1573 (CH aromatic, C=N, NH_2); 1511 (N=C-S); 1169 (C-S).

$C_{11}H_{11}N_5OS$ (261.31) Calc. C 50.56 H 4.24 N 26.80 S 12.26
Found C 50.76 H 4.34 N 26.58 S 12.31

2b: Method B: To a suspension of **1** (2 mmol) and $NaHCO_3$ (2 mmol) in dry 1,2-dimethoxyethane (50 ml) a solution of acetyl chloride (2 mmol) in dry 1,2-dimethoxyethane (20 ml) is added dropwise. After 2 h stirring at r.t. the mixture is heated under reflux for a few minutes. The precipitate formed is filtered off, washed with water and dried.

Yield 72% (A), 57% (B), mp 197–198 °C, orange needles. ^{1}H NMR (DMSO-d_6): δ(ppm) 2.73 (s, 3H, CH_3); 3.82 (s, 3H, OCH_3); 7.00 (m, 2H, C_6H_4-3′); 7.24 (s, 2H, NH_2); 7.88 (m, 2H, C_6H_4-2′); 8.38 (s, 1H, CH=N). ^{13}C NMR (DMSO-d_6): δ(ppm) 15.4 (CH_3); 55.5 (OCH_3); 114.3 (C_6H_4-3′); 127.8 (C_6H_4-1′); 130.0 (C_6H_4-2′); 151.5 (N-C=N); 155.4 (CH=N); 161.4 (C_6H_4-4′); 165.1 (S-C=N); 167.7 (S-C(R)=N). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3485, 3392, 3332 (NH_2); 1619, 1605, 1598, 1573 (CH aromatic, C=N, NH_2); 1511 (N=C-S); 1166 (C-S).

$C_{12}H_{13}N_5OS$ (275.33) Calc. C 52.34 H 4.75 N 25.43 S 11.64
Found C 52.57 H 4.76 N 25.42 S 11.65

2c: Yield 77% (A), mp 132–133 °C, orange needles. ^{1}H NMR (DMSO-d_6): δ(ppm) 1.35 (t, 3H, CH_3); 3.13 (q, 2H, CH_2); 3.82 (s, 3H, OCH_3); 7.00 (m, 2H, C_6H_4-3′); 7.23 (s, 2H, NH_2); 7.89 (m, 2H, C_6H_4-2′); 8.34 (s, 1H, CH=N). ^{13}C NMR (DMSO-d_6): δ(ppm) 14.2 (CH_3); 23.2 (CH_2); 55.5 (OCH_3); 114.3 (C_6H_4-3′); 127.8 (C_6H_4-1′); 130.0 (C_6H_4-2′); 151.5 (N-C=N); 155.4 (CH=N); 161.4 (C_6H_4-4′); 164.6 (S-C=N); 174.0 (S-C(R)=N). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3477, 3431, 3320, 3209 (NH_2); 1617, 1606, 1573 (CH aromatic, C=N, NH_2); 1512 (N=C-S); 1164 (C-S).

$C_{13}H_{15}N_5OS$ (289.35) Calc. C 53.96 H 5.22 N 24.20 S 11.07
Found C 53.14 H 5.40 N 23.86 S 10.86

2d: Yield 82% (A), mp 166–167 °C, orange needles. ^{1}H NMR (DMSO-d_6): δ(ppm) 3.81 (s, 3H, OCH_3); 7.00 (m, 2H, C_6H_4-3′); 7.31 (s, 2H, NH_2); 7.60 (m, 3H, C_6H_5); 7.92 (m, 2H, C_6H_4-2′); 8.06 (m, 2H, C_6H_5); 8.40 (s, 1H, CH=N). ^{13}C NMR (DMSO-d_6): δ(ppm) 55.5 (OCH_3); 114.3 (C_6H_4-3′); 127.7 (C_6H_4-1′); 128.1 (C_6H_5-2″); 129.5 (C_6H_5-1″); 129.7 (C_6H_5-3″); 130.1 (C_6H_4-2′); 131.9 (C_6H_5-4″); 151.4 (N-C=N); 155.6 (CH=N); 161.4 (C_6H_4-4′); 164.8 (S-C=N); 169.8 (S-C(R)=N). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3520, 3409, 3210 (NH_2); 1624, 1604, 1590, 1569 (CH aromatic, C=N, NH_2); 1510 (N=C-S); 1168 (C-S).

$C_{17}H_{15}N_5OS$ (337.39) Calc. C 60.51 H 4.48 N 20.75 S 9.50
Found C 60.37 H 4.53 N 20.64 S 9.16

Thiooxalic Acid 2-Amide-1-(2-benzoylhydrazide)-2-[2-(4-methoxybenzylidene)hydrazones] *3a–d*

General Procedure

To a solution of **1** (2 mmol) in dry methanol (40 ml) $NaHCO_3$ (2 mmol) is added and than dropwise a solution of corresponding aromatic acyl chloride (2 mmol) in dry methanol (20 ml). After 3 h stirring at r.t., the mixture is heated under reflux for 1 h. The precipitate formed is filtered off and washed with water and ethanol.

3a: Yield 78%, mp 263–265 °C, yellow crystals. ^{1}H NMR (DMSO-d_6): δ(ppm) 3.84 (s, 3H, OCH_3); 7.05 (m, 2H, C_6H_4-3′); 7.59 (m, 3H, C_6H_5-3″,4″); 7.88 (m, 2H, C_6H_5-2″); 7.93 (m, 2H, C_6H_4-2′); 8.70 (s, 1H, CH=N); 9.04, 9.36 (2s, 2 × 1H, NH_2); 11.30 (s, 1H, NH); 12.30 (b, 1H, NH^+). ^{13}C NMR (DMSO-d_6): δ(ppm) 55.5 (OCH_3); 114.4 (C_6H_4-3′); 125.7 (C_6H_4-1′); 126.9 (C_6H_5-2″); 129.1

(C_6H_5-3″); 130.5 (C_6H_4-2′); 131.9 (C_6H_5-4″); 133.9 (C_6H_5-1″); 153.9 (CH=N); 156.9 (S^--C=N); 157.5 (N-C=N); 161.7 (C=O); 162.2 (C_6H_4-4′). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3422, 3368, 3248, 3182, 3152 (NH_2, NH); 1668, 1651, 1605, 1578 (CH aromatic, C=N, C=O, NH, NH_2); 1514 (N=C-S); 1172 (C-S).

$C_{17}H_{17}N_5O_2S$ (355.41) Calc. C 57.45 H 4.82 N 19.70 S 9.02
Found C 57.30 H 4.84 N 19.51 S 9.00

3b: Yield 72%, mp 267–269 °C, yellow crystals. ^{1}H NMR (DMSO-d_6): δ(ppm) 2.39 (s, 3H, CH_3); 3.84 (s, 3H, OCH_3); 7.04 (m, 2H, C_6H_4-3′); 7.37 (d, 2H, C_6H_4-3″); 7.78 (d, 2H, C_6H_4-2″); 7.92 (m, 2H, C_6H_4-2′); 8.69 (s, 1H, CH=N); 8.96, 9.28 (2s, 2 × 1H, NH_2); 11.28 (b, 1H, NH); 12.30 (b, 1H, NH^+). ^{13}C NMR (DMSO-d_6): δ(ppm) 21.2 (CH_3); 55.6 (OCH_3); 114.5 (C_6H_4-3′); 125.8 (C_6H_4-1′); 127.0 (C_6H_4-2″); 129.6 (C_6H_4-3″); 130.5 (C_6H_4-2′); 131.1 (C_6H_4-1″); 142.0 (C_6H_4-4″); 153.8 (CH=N); 156.6 (S^--C=N); 157.6 (N-C=N); 161.6 (C=O); 162.1 (C_6H_4-4′). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3425, 3292, 3246, 3160 (NH_2, NH); 1654, 1605, 1572 (CH aromatic, C=N, C=O); 1514 (N=C-S); 1172 (C-S).

$C_{18}H_{19}N_5O_2S$ (369.44) Calc. C 58.52 H 5.18 N 18.95 S 8.67
Found C 58.15 H 5.23 N 18.89 S 8.63

3c: Yield 55%, mp 290–291 °C, yellow crystals. ^{1}H NMR (DMSO-d_6): δ(ppm) 3.84 (s, 3H, OCH_3); 7.04 (m, 2H, C_6H_4-3′); 7.80 (m, 4H, C_6H_4-2″,3″); 7.93 (m, 2H, C_6H_4-2′); 8.70 (s, 1H, CH=N); 9.02, 9.35 (2s, 2 × 1H, NH_2); 11.30 (b, 1H, NH); 12.40 (b, 1H, NH^+). ^{13}C NMR (DMSO-d_6): δ(ppm) 55.6 (OCH_3); 114.5 (C_6H_4-3′); 125.7 (C_6H_4-1′); 129.0 (C_6H_4-2″); 130.5 (C_6H_4-2′); 132.2 (C_6H_4-3″); 132.9 (C_6H_4-1″); 154.0 (CH=N); 157.4 (S^--C=N); 157.5 (N-C=N); 160.8 (C=O); 162.2 (C_6H_4-4′). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3428, 3390, 3246, 3164 (NH_2, NH); 1663, 1605, 1591, 1572 (CH aromatic, C=N, C=O, NH_2); 1513 (N=C-S); 1172 (C-S).

$C_{17}H_{16}BrN_5O_2S$ (434.30) Calc. C 47.01 H 3.71 N 16.12 S 7.38
Found C 47.00 H 3.72 N 16.11 S 7.31

3d: Yield 70%, mp 280–282 °C, yellow crystals. ^{1}H NMR (DMSO-d_6): δ(ppm) 3.84 (s, 3H, OCH_3); 7.05 (m, 2H, C_6H_4-3′); 7.64 (m, 2H, C_6H_4-3″); 7.90 (m, 2H, C_6H_4-2″); 7.93 (m, 2H, C_6H_4-2′); 8.70 (s, 1H, CH=N); 9.05, 9.36 (2s, 2 × 1H, NH_2); 11.30 (s, 1H, NH); 12.33 (b, 1H, NH^+). ^{13}C NMR (DMSO-d_6): δ(ppm) 55.6 (OCH_3); 114.5 (C_6H_4-3′); 125.7 (C_6H_4-1′); 128.9 (C_6H_4-3″); 129.3 (C_6H_4-2″); 130.5 (C_6H_4-2′); 132.6 (C_{6H_4}-1″); 136.8 (C_6H_4-4″); 154.0 CH=N); 157.3

(S^--C=N); 157.5 (N-C=N); 160.7 (C=O); 162.2 (C_6H_4-4′). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3418, 3245, 3154 (NH_2, NH); 1661, 1605, 1571, 1548 (CH aromatic, C=N, C=O, NH_2); 1513 (N=C-S); 1172 (C-S).

$C_{17}H_{16}ClN_5O_2S$ (389.85) Calc. C 52.37 H 4.13 N 17.96 S 8.22
Found C 52.03 H 4.23 N 17.77 S 8.26

2,3-Dihydro-2-thiono-1,3,4-thiadiazole-5-[2-(4-methoxybenzylidene)carboxamide hydrazone] *4*

Method A: To a suspension of **1** (2 mmol) in methanol (80 ml) a solution of CS_2 (3 mmol) in methanol (10 ml) is added dropwise. After 1 h stirring at r.t., the mixture is heated under reflux for 4 h. After cooling of the mixture to r.t., the precipitate is filtered off and washed with ethanol. A further purification of the obtained product can be performed by his recrystallization from hot ethanol.

Method B: CS_2 (2 ml) is added to a suspension of **1** (2 mmol) in methanol (1 ml). After stirring 1 h at r.t., the mixture is heated shortly. Then the reaction mixture is worked up as described before.

Yield 75% (A)/90% (B), mp 225 °C, brownish crystals. ^{1}H NMR (DMSO-d_6): δ(ppm) 3.80 (s, 3H, OCH_3); 6.98 (m, 2H, C_6H_4-3′); 7.18 (b, 2H, NH_2); 7.86 (m, 2H, C_6H_4-2′); 8.34 (s, 1H, CH=N); 14.80 (b, 1H, NH). ^{13}C NMR (DMSO-d_6): δ(ppm) 55.5 (OCH_3); 114.3 (C_6H_4-3′); 127.6 (C_6H_4-1′); 130.2 (C_6H_4-2′); 150.0 (N-C=N); 156.1 (CH=N); 156.5 (S-C=N); 161.5 (C_6H_4-4′); 189.4 (C=S). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3458, 3331, 3206 (NH_2, NH); 1625, 1604, 1576 (CH aromatic, C=N, NH_2); 1540 (N-C-S); 1166 (C-S).

$C_{11}H_{11}N_5OS_2$ (293.36) Calc. C 45.03 H 3.77 N 23.87 S 21.85
Found C 45.40 H 3.88 N 23.65 S 21.88

2,3-Dihydro-2-oxo-5-[2-(4-methoxybenzylidene)carboxamide hydrazone] *5*

To a solution of **1** (2 mmol) in dry 1,2-dimethoxyethane (50 ml) a solution of 1,1′-carbonyldiimidazole (2 mmol) in dry 1,2-dimethoxyethane (20 ml) is added dropwise. The reaction mixture is stirred 3 h at r.t., the precipitate is filtered off, washed with petroleum ether and dried.

Yield 72%, mp 261–263 °C, yellow crystals. ^{1}H NMR (DMSO-d_6): δ(ppm) 3.84 (s, 3H, OCH_3); 7.00 (m, 2H, C_6H_4-3′); 7.00 (b, 2H, NH_2); 7.88 (m, 2H, C_6H_4-2′); 8.36 (s, 1H, CH=N); 13.30 (b, 1H, NH). ^{13}C NMR (DMSO-d_6): δ(ppm) 55.5 (OCH_3); 114.3 (C_6H_4-3′); 127.7 (C_6H_4-1′); 130.1 (C_6H_4-2′); 148.4 (S-C=N); 151.3 (N-C=N); 155.6 (CH=N); 161.4 (C_6H_4-4′); 171.9 (C=O). IR

(KBr): $\tilde{\nu}$ (cm^{-1}) = 3462, 3355, 3150 (NH_2, NH); 1655 (C=O); 1618, 1601, 1575 (CH aromatic, C=N, NH_2); 1510 (N-C-S); 1168 (C-S).

$C_{11}H_{11}N_5O_2S$ (277.30) Calc. C 47.64 H 3.99 N 25.25 S 11.56
Found C 47.60 H 4.19 N 24.92 S 11.38

Crystal Structure Determination

Crystals of **2a** and **2b** were measured on a Siemens P4 four circle diffractometer after taking rotational photos and determining the unit cells in automatic mode. The structures were solved by direct methods (Siemens SHELXTL, Copyright

TABLE I Crystal and structure solution data for compounds **2a** and **2b**

	2a	*2b*
Formula	$C_{11}H_{11}N_5OS$	$C_{12}H_{13}N_5OS$
M [g·mol^{-1}]	261.31	275.33
Crystal size [mm]	0.86 × 0.24 × 0.06	0.70 × 0.20 × 0.06
Crystal system	monoclinic	monoclinic
Space group (No. I.T.)	$P2_1/c$ (14)	$P2_1/c$ (14)
a [Å]	15.263(3)	10.911(2)
b [Å]	5.316(1)	5.284(1)
c [Å]	15.823(3)	23.373(5)
α [°]	90	90
β [°]	102.69(3)	91.92(3)
γ [°]	90	90
V [Å^3]	1252.5(4)	1346.8(5)
Z	4	4
$\rho_{calcd.}$ [g·cm^{-3}]	1.386	1.358
μ (Mo-K_α) [cm^{-1}]	2.54	2.40
F(000) e	544	576
Temperature [°C]	25	25
Radiation	λ = 0.71073 Å (Mo-K_α), graphite monochromator	
Diffractometer	Siemens P4	
Data collecting mode	ω-scan	
Scan range (2Θ) [°]	5.28–45	5.02–45
hkl range	0/17, 0/6, −18/18	0/12, 0/6, −27/27
Measured refl.	1708	1861
Unique refl.	1636	1753
Observed refl.	1246	1177
Observ. criterion I>	2σ (I)	
Refined param.	172	180
R1 for obs. refl.	0.0487	0.0585
R1 for all	0.0685	0.0979
wR2 for all	0.1375	0.1677
restrained GooF	1.046	1.028
Δρ (max/min) [e·Å^{-3}]	0.164/−0.239	0.278/−0.310

1990, Siemens Analytical Xray Inst. Inc.) and refined by the full-matrix least squares method of SHELXL-93.[12] All non-hydrogen atoms were refined anisotropically. Although some hydrogen positions could be seen from the difference Fourier map, all hydrogens were put into their theoretical positions and refined using the "riding model". The most important date can be seen from Table I.

The weighting scheme was calculated according to $w = 1/[\sigma^2 (Fo^2) + (0.0498P)^2 + 0.1948P]$ for **2a** and $w = 1/[\sigma^2 (Fo^2) + (0.0662P)^2 + 0.3009P]$ for **2b** with $P = (Fo^2 + 2Fc^2)/3$ in both cases.

For the last steps of refinement the reflection to parameter ratio was 1633/172 for **2a** and 1751/180 for **2b**. Both structures are very similar with respect to bond lengths, angles and least square planes. But also the intermolecular arrangement shows similarities. So there are dimeric subunits due to pairwise hydrogen bonds between a hydrogen at N3 and N1 in the thiadiazole ring, the N...H distances being 2.335 (**2a**) and 2.409 Å (**2b**).

Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft fuer wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-391048 and CSD-391049, the names of the authors, and the journal citation.

References

[1] H. Dehne, A. Scheunemann, M. Michalik, H. Hartung, F. Heinemann and H. U. Kibbel, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **86**, 177 (1994).
[2] F. W. Heinemann, H. Hartung, H. Dehne and A. Scheunemann, *Acta Cryst.*, **C51**, 442 (1995).
[3] H. Dehne, A. Scheunemann, M. Michalik, H. Hartung and F. Heinemann, *Sulfur Lett.*, **18**, 135 (1995).
[4] K. J. Reubke, in Houben-Weyl: *Methoden der organischen Chemie, Bd. E8d/4* (Georg-Thieme-Verlag, Stuttgart, New York, 1994) 4th ed., pp. 189–304.
[5] W. R. Sherman, *Heterocycl. Compd. (R. C. Elderfield, Ed.)*, **7**, 587 (1961).
[6] H. Eilingsfeld, *Chem. Ber.*, **98**, 1308 (1965).
[7] K. A. Jensen and C. Pedersen, *Acta Chem. Scand.*, **15**, 1124 (1961).
[8] L. B. Kier and M. K. Scott, *J. Heterocycl. Chem.*, **5**, 277 (1968); C. A. **68**, 114508 (1968).
[9] R. Grashey, M. Baumann and W.-D. Lubos, *Tetrahedron Lett.*, **1968**, 5881.
[10] A. Ya. Lazaris and A. N. Egorochkin, *Zh. Org. Khim.*, **6**, 2342 (1970); C. A. **74**, 42317 (1971).
[11] P. Stelzel, in Houben-Weyl: *Methoden der organischen Chemie, Bd. 15/2* (Georg-Thieme-Verlag, Stuttgart, 1974) 4th ed., pp. 326–331.
[12] G. M. Sheldrick, *SHELXL-93*, Universität Göttingen (1993).