Alkylation of Zwitterionic Thiooxalic Acid Derivatives

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Abstract: The new S-alkyl thiooxal-1-hydrazono-2-amidrazonium halides 2-4 were synthesized by reaction of the corresponding zwitterionic thiooxalic acid derivatives 1 with alkyl halides in methanol. The structures of compounds 4b and 4d were proven by X-ray structural analysis. Both compounds form an interesting intermolecular network of hydrogen bonds in the solid state.

Keywords: Alkylation, thiooxalic acid derivatives, halides, X-ray analysis.

Introduction

Generally thiocarboxamides and their anions react with alkyl halides in kinetically controlled reactions at the S-atom. With alkylating agents which first form stable carbenium ions, direct N-alkylation was observed. However, in the alkylation reactions of alkane and arene thiocarboxylic acid hydrazides only S-alkylation has been found [1]. 1,4-Dihydotetrazines were formed by self-condensation and elimination of alkanethiol from the thiocarboxylic acid S-alkyl ester hydrazonides, which were obtained by reaction of N-unsubstituted thiohydrazides with alkyl halides in alkaline medium [2]. The S-alkylation products of N²-mono- and N²,N²-disubstituted thiocarboxylic acid...
hydrazides were thermally more stable [1]. Some years ago we synthesized the new zwitterionic thiooxalic acid 2-amide-1-hydrazide-2-hydrazone (1a) [3] and the methyl (1b) and phenyl derivative (1c), respectively [4]. These compounds are multifunctional building blocks especially for heterocycles [5,6]. Here we describe reactions of the substances 1a-c with several alkyl halides and discuss some structural data of the new alkylation products.

Results and Discussion

The zwitterionic thiooxalic acid derivatives 1a-c reacted in methanol with several alkyl halides to give the yellow S-alkyl-thiooxal-1-hydrazone-2-amidrazonium halides 2-4 in good yields (Scheme 1).

**Scheme 1. Synthesis of the halides 2-4**

While the educts 1a and 1b only needed 4 h under reflux to react (Experimental, Method A) the more stable phenyl derivative 1c had to be heated for 12 h (Experimental, Method B). The reaction was performed in the absence of a strong base like potassium hydroxide because compounds 2-4 are unstable under these conditions. The best yields of the products were obtained with alkyl bromides and iodides (Table 1) but not with the corresponding chlorides.

**Table 1. Analytical data of the halides 2-4**

| Compd. | Formula (M.w.) | R¹ | R² | X | M.p. °C | Yield % | Calculated/Found % | %C | %H | %N | %S |
|--------|----------------|-----|-----|----|---------|----------|--------------------|-----|-----|-----|-----|
| 2a     | C₃H₁₀I₅N₅S   | H   | CH₃ | I  | 119-120 | 59       | 13.09 3.66 25.45 11.65 | 13.34 3.65 25.41 11.65 |
| 2b     | C₉H₁₅BrN₆O₂S | H   | 4-NO₂C₆H₄CH₂ | Br | 92-94   | 72       | 30.95 3.75 24.06 9.18   | 30.74 3.73 23.51 9.13   |
Table 1. Continued

| 3   | C_{11}H_{17}BrN_{6}O_{2}S  | CH_{3}  | 4-NO_{2}C_{6}H_{4}CH_{2} | Br    | 87-90 | 4.54 | 22.28 | 8.50 |
|-----|---------------------------|---------|--------------------------|-------|-------|------|-------|------|
|     | (377.26)                  |         |                          |       | 92    |      |       |      |
| 4a  | C_{13}H_{18}IN_{5}S        | C_{6}H_{5} |                         | I     | 196-200 | 4.25 | 16.39 | 7.50 |
|     | (427.30)                  | CH_{3}  |                          |       | 62    |      |       |      |
|     |                           |         |                          |       |       |      |       |      |
| 4b  | C_{16}H_{20}IN_{5}S        | C_{6}H_{5} |                         | I     | 195-200 | 4.57 | 15.87 | 7.26 |
|     | (441.33)                  | C_{2}H_{5} |                          |       | 65    |      |       |      |
|     |                           |         |                          |       |       |      |       |      |
| 4c  | C_{24}H_{38}BrN_{5}S       | C_{6}H_{5} |                         | Br    | 75-80 | 7.16 | 13.83 | 6.33 |
|     | (506.54)                  | CH_{3}(CH_{2})_{9} |                          |       | 78    |      |       |      |
|     |                           |         |                          |       |       |      |       |      |
| 4d  | C_{21}H_{22}BrN_{5}S       | C_{6}H_{5} |                         | Br    | 205-209 | 4.86 | 15.34 | 7.02 |
|     | (456.41)                  | C_{6}H_{5}CH_{2} |                          |       | 40    |      |       |      |
|     |                           |         |                          |       |       |      |       |      |
| 4e  | C_{21}H_{21}BrN_{6}O_{2}S  | C_{6}H_{5} |                         | Br    | 140-145 | 4.22 | 16.76 | 6.39 |
|     | (501.40)                  | 4-NO_{2}C_{6}H_{4}CH_{2} |                          |       | 67    |      |       |      |

The structures given for 2-4 are consistent with the spectroscopic data. Thus, in the $^1$H,$^1$H COSY spectrum of 4a a correlation between the C$_6$H$_5$NHNH and C$_6$H$_5$NHNH protons was observed. In the HMBC spectrum of 4a correlations were found between C-1’ and the C$_6$H$_5$NHNH proton as well as S-C=N and the CH$_3$ protons, respectively (see Experimental). Thus, a distinction between the NH protons and the phenyl group signals could be made.

**Figure 1.** Arrangement of molecules of 4b in the crystal lattice
X-ray structure investigations of the educt 1c and of the alkylation products 4b and 4d (see Figures 1 and 2, Table 2) demonstrate that the original conformation in the crystal of 1c [4] is rearranged in these alkylation products. Both compounds form an interesting intermolecular network of hydrogen bonds in the solid state. While the dominating motif in 4b consists of three organic molecules around one iodide with N(3)H(3), N(4)H(4B), N(5)H(5) as donor groups (see Figure 1, Table 3), the bromide in 4d is surrounded by four molecules (see Figure 2, Table 4).

**Figure 2.** Arrangement of molecules of 4d in the crystal lattice

Each molecule provides another NH function so that all four NH-groups participate in the two-dimensional network. A similar structure was already investigated earlier: the corresponding compound S-(methoxycarbonylmethyl)-thiooxal-1-(2-phenylhydrazono)-2-(2-phenylamidrazonium) bromide resulted from the reaction of 1c with methyl bromoacetate [5].
Table 2. Crystal structure data.

| Compound | 4b | 4d |
|----------|----|----|
| Empirical formula | C₁₆H₂₀IN₅S | C₂₁H₂₂BrN₅S |
| Formula weight | 441.33 | 456.41 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | C2/c | P2₁/n |
| Unit cell dimensions [Å] | | |
| a = 22.963(5) | 13.391(3) |
| b = 13.236(3) | 10.928(3) |
| c = 16.537(3) | 15.504(3) |
| β = 132.44(3)° | β = 111.03(2)° |
| Volume [Å³] | 3709.3(13) | 2117.7(9) |
| ρ (calculated) [g cm⁻³] | 1.581 | 1.432 |
| Z | 8 | 4 |
| F (000) | 1760 | 936 |
| μ(Mo-Kα) [mm⁻¹] | 1.845 | 2.056 |
| Crystal size [mm] | 0.52 x 0.44 x 0.24 | 0.52 x 0.39 x 0.30 |
| 2Θ range | 3.9/44 | 4.68/45.98 |
| hkl range | -24/1, -1/13, -13/17 | -1/14, -12/1, -17/16 |
| Measured refl. | 2750 | 3747 |
| Unique refl. | 2271 | 2910 |
| Observed refl. | 1948 | 2231 |
| Completeness to Θ = 22.00° | 99.9% | 99.2% |
| Data / restraints / parameters | 2271 / 0 / 228 | 2910 / 0 / 257 |
| Min. transm. | 0.59421 | 0.12686 |
| Max. transm. | 0.83244 | 0.16969 |
| R1 for observed refl. | 0.0350 | 0.0433 |
| R1 for all refl. | 0.0417 | 0.0643 |
| wR2 for all refl. | 0.0930 | 0.1097 |
| GoF on F² | 1.022 | 1.009 |
| ρ (max/min) [e.Å⁻³] | 0.374 / -0.442 | 0.319 / -0.426 |

Table 3. Selected bond lengths [in Å], bond angles [in °] and torsion angles [in °] for compound 4b

| Bond | 4b | 4d |
|------|----|----|
| S(1)-C(1) | 1.763(5) | 1.315(7) |
| N(1)-C(1) | 1.302(6) | 1.462(7) |
| N(1)-N(2) | 1.313(6) | 3.019(7) |
| N(3)-C(2) | 1.311(7) | 2.59 |
| N(3)-N(5) | 1.408(7) | 2.959(5) |
Table 3. Continued

| Bond or Angle | Distance/Angle | Distance/Angle | Distance/Angle | Distance/Angle |
|---------------|---------------|---------------|---------------|---------------|
| N(4)-C(2)-C(1) | 119.0(6) | N(4)-H(4B)...I(1)#2 | 3.539(6) | C(2)-C(1)-S(1) | 120.6(4) |
| N(2)-N(1)-C(1)-C(2) | -177.8(4) | H(4B)...I(1)#2 | 2.96 | N(5)-N(3)-C(2)-C(1) | 178.0(5) |
| N(2)-N(1)-C(1)-S(1) | 1.7(6) | N(3)-H(3)...I(1)#3 | 3.518(5) | N(1)-C(1)-C(2)-N(3) | -3.1(7) |
| N(5)-N(3)-C(2)-N(4) | -3.7(8) | H(3)...I(1)#3 | 2.83 | S(1)-C(1)-C(2)-N(3) | 177.4(4) |
| N(4)-H(4B)...N(5) | 2.678(9) | C(1)-N(1)-N(2) | 119.5(4) | N(1)-C(1)-C(2)-N(4) | 178.7(5) |
| H(4B)...N(5) | 2.34 | C(2)-N(3)-N(5) | 119.6(5) | S(1)-C(1)-C(2)-N(4) | -0.9(6) |
| N(5)-H(5)...I(1)#1 | 3.989(6) | N(1)-C(1)-C(2) | 115.1(4) | | |
| H(5)...I(1)#1 | 3.21 | N(1)-C(1)-S(1) | 124.3(4) | | |

Standard deviations in parentheses. Symmetry transformations used to generate equivalent atoms: #1 x+1/2,-y-1/2,z+1/2    #2 -x+1/2,y-1/2,-z+1/2     #3 -x+1/2,-y-1/2,-z+1

Table 4. Selected bond lengths [in Å], bond angles [in °] and torsion angles [in °] for compound 4d

| Bond or Angle | Distance/Distance | Distance/Distance | Distance/Distance |
|---------------|-------------------|-------------------|-------------------|
| S(1)-C(1) | 1.750(4) | H(4B)...Br(1)#1 | 2.77 | N(4)-C(2)-N(3) | 120.1(4) |
| N(4)-C(2) | 1.297(6) | N(2)-H(2)...Br(1) | 3.683(4) | N(4)-C(2)-C(1) | 121.5(4) |
| N(1)-C(1) | 1.310(5) | H(2)...Br(1) | 2.89 | N(3)-C(2)-C(1) | 118.3(4) |
| N(1)-N(2) | 1.313(5) | N(3)-H(3)...Br(1)#2 | 3.343(4) | N(1)-C(1)-C(2)-N(4) | 159.2(4) |
| N(3)-C(2) | 1.327(6) | H(3)...Br(1)#2 | 2.51 | S(1)-C(1)-C(2)-N(4) | -16.6(6) |
| N(3)-N(5) | 1.402(5) | N(5)-H(5)...Br(1)#3 | 3.470(4) | N(1)-C(1)-C(2)-N(3) | -17.9(6) |
| C(1)-C(2) | 1.466(6) | H(5)...Br(1)#3 | 2.83 | S(1)-C(1)-C(2)-N(3) | 166.2(3) |
| N(4)-H(4A)...S(1)#1 | 3.353(4) | C(1)-N(1)-N(2) | 120.7(4) | N(2)-N(1)-C(1)-C(2) | -179.5(4) |
| H(4A)...S(1)#1 | 2.75 | C(2)-N(3)-N(5) | 119.7(4) | N(2)-N(1)-C(1)-S(1) | -4.0(6) |
| N(4)-H(4B)...S(1) | 3.061(4) | N(1)-C(1)-C(2) | 113.8(4) | N(5)-N(3)-C(2)-N(4) | 1.1(7) |
| H(4B)...S(1) | 2.64 | N(1)-C(1)-S(1) | 126.4(3) | N(5)-N(3)-C(2)-C(1) | 178.3(4) |
| N(4)-H(4B)...Br(1)#1 | 3.454(4) | C(2)-C(1)-S(1) | 119.6(3) | | |

Standard deviations in parentheses. Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,y+1/2,-z+1/2    #2 -x+1,-y+1,-z+1    #3 x,y+1,z

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Experimental

General

Melting points were determined with a Boëtius micro heating stage (Carl Zeiss Jena). Elemental analyses were performed with a CHNS-932 LECO analyzer. IR spectra were recorded on a Nicolet Protégé 460 FT-IR spectrometer. 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 AC 250 and ARX 300 spectrometers. The calibration of spectra was carried out by means of solvent peaks (DMSO-d$_6$: $\delta^1$H = 2.50; $\delta^{13}$C = 39.7). The assignment of signals were confirmed by DEPT and two-dimensional correlation spectra.

Method A: Preparation of halides 2

To a suspension of thiooxalic acid 2-amide 1-hydrazide 2-hydrazone (1a) (0.67 g, 5 mmol) in methanol (50 mL) a solution of methyl iodide or 4-nitrobenzyl bromide in methanol (20 mL) was added dropwise at r.t. The mixture was stirred at r.t. for 1 h and then heated under reflux for 4 h. After removing the solvent under reduced pressure a yellow oil was obtained. The addition of a small amount of ethanol gives yellow crystals which were filtered and dried. In case of 2b the unconverted 4-nitrobenzyl bromide can be removed by addition of water (50 mL) to the oil, filtration of the solution and evaporation of the solvent.

$S$-Methyl-thiooxal-1-hydrazono-2-amidrazonium iodide (2a)

$$\begin{align*}
\text{H}_2\text{C} & \text{-S} \\
\text{H}_2\text{N} & \text{-N} \\
& \text{+ I}^-
\end{align*}$$

IR (KBr): $\tilde{\nu}$ (cm$^{-1}$) = 3467, 3317, 3210, 3125 (NH, NH$_2$); 2992, 2914 (CH$_3$); 1681, 1605, 1597, 1557, 1505 (C=N, NH, NH$_2$); 1484 (S-C=N); MS (70 eV/EI): m/z (%) = 147 (M$^+$-HI, 35); 128 (100); $^1$H-NMR (250.1 MHz, DMSO-d$_6$): $\delta$ = 10.14 (s, 1H, NH$_2$NH); 9.08 (s, 2H), 8.37 (s, 2H), 5.03 (s, 2H, NH$_2$); 2.14 (s, 3H, CH$_3$). $\cdot^{13}$C NMR (62.9 MHz, DMSO-d$_6$): $\delta$ = 159.1 (N-C-N); 117.2 (S-C-N); 14.4 (CH$_3$).

$S$-(4-Nitrobenzyl)thiooxal-1-hydrazono-2-amidrazonium bromide (2b)

$$\begin{align*}
\text{O}_2\text{N} & \text{-S} \\
\text{H}_2\text{N} & \text{-N} \\
& \text{+ Br}^-
\end{align*}$$
IR (KBr): $\tilde{\nu}$ (cm$^{-1}$) = 3413, 3318, 3296, 3230 (NH, NH$_2$); 3106 (C$_6$H$_4$); 2935, 2847 (CH$_2$); 1672, 1602, 1564 (C=N, NH, NH$_2$); 1519 (NO$_2$); 1504 (S=C=N); 1431 (NO$_2$); MS (70 eV/EI): $m/z$ (%) = 269 (M$^+$-HBr, 12); 170 (100); $^1$H-NMR (250.1 MHz, DMSO-$d_6$): $\delta$ = 10.03 (br, 1H, NH$_2$NH); 9.22 (s, 2H), 8.22 (s, 2H, NH$_2$); 7.57 (m, 2H, H-2''); 8.13 (m, 2H, H-3''); 4.98 (s, 2H, NH$_2$); 4.06 (s, 2H, CH$_2$); $^{13}$C-NMR (62.9 MHz, DMSO-$d_6$): $\delta$ = 159.1 (N-C-N); 146.8 (C-4''); 145.1 (C-1'''); 130.6 (C-2''); 123.6 (C-3''); 114.1 (S-C=N); 34.5 (CH$_2$).

**Method B: Preparation of halides 3 and 4**

To a suspension of zwitterionic compound 1b or 1c (3 mmol) in methanol (20 mL) a solution of the corresponding alkylating agent in methanol (50 mL) was added dropwise at r.t. The mixture was stirred under reflux (3: 4 h, 4: 12 h). Then the solvent was evaporated under reduced pressure. In the case of 3 addition of water to the resulting oil and leaving the mixture at 6 °C for 14 days gave yellow crystals. Compounds 4 crystallized during removing the solvent without any further manipulation. The products were purified by recrystallization (3 from ethanol, 4 from water). Purification of 4c was not necessary.

*S-(4-Nitrobenzyl)thiooxal-1-(2-methylhydrazono)-2-(2-methylamidrazonium)bromide (3)*

![Chemical structure of 3]

IR (KBr): $\tilde{\nu}$ (cm$^{-1}$) = 3491, 3411, 3368, 2798 (NH, NH$_2$); 1642, 1597, 1578 (C=N); 1511 (NO$_2$); 1462 (S-C=N); 1340 (NO$_2$); MS (70 eV/EI): $m/z$ (%) = 296 (M$^+$-HBr, 27); 28 (100); $^1$H-NMR (250.1 MHz, DMSO-$d_6$): $\delta$ = 9.84 (s, 1H, CH$_3$NHNH); 9.36 (q, 1H, CH$_3$NH); 8.29 (s, 1H), 8.18 (s, 1H, NH$_2$); 8.14 (m, 2H, H-3''); 7.53 (m, 2H, H-2''); 5.27 (br, 1H, CH$_3$NH); 4.04 (s, 2H, CH$_2$); 3.22 (d, 3H, CH$_3$, $J = 3.5$ Hz); 2.35 (s, 3H, CH$_3$); $^{13}$C-NMR (62.9 MHz, DMSO-$d_6$): $\delta$ = 159.1 (N-C-N); 146.8 (C-4''); 145.1 (C-1'''); 130.8 (C-2''); 123.6 (C-3''); 109.1 (S-C=N); 38.2 (CH$_3$); 37.3 (CH$_3$); 34.6 (CH$_2$).

*S-Methyl-thiooxal-1-(2-phenylhydrazono)-2-(2-phenylamidrazonium)iodide (4a)*

![Chemical structure of 4a]
IR (KBr): $\tilde{\nu}$ (cm$^{-1}$) = 3384, 3285 (NH$_2$); 3171 (NH); 1645 (C=N); 1515; 1469; 1240; 758; MS (70 eV/EI): $m/z$ (%) = 299 (M$^+$-HI, 100); $^1$H-NMR (300.1 MHz, DMSO-d$_6$): $\delta$ = 11.12 (s, 1H, C$_6$H$_5$NHNH); 11.02 (s, 1H, C$_6$H$_5$NHNH); 9.31 (s, 1H, NH$_2$); 8.47 (s, 1H, C$_6$H$_5$NHN); 7.72 (m, 2H, H-2'); 7.36 (m, 2H, H-3'); 7.29 (m, 2H, H-3); 7.06 (m, 1H, H-4'); 6.91 (m, 1H, H-4); 6.88 (m, 1H, H-2'); 2.36 (s, 3H, CH$_3$); $^{13}$C-NMR (75.5 MHz, DMSO-d$_6$): $\delta$ = 160.6 (N-C-N); 146.8 (C-1); 142.5 (C-1'); 129.3, 129.2 (C-3, C-3'); 123.6 (C-4'); 120.9 (C-4); 119.5 (S=C=N); 116.1 (C-2'); 113.7 (C-2); 15.9 (CH$_3$).

S-Ethyl-thiooxal-1-(2-phenylhydrazono)-2-(2-phenylamidrazonium)iodide (4b)

IR (KBr): $\tilde{\nu}$ (cm$^{-1}$) = 3397, 3286 (NH$_2$); 3176 (NH); 1645 (C=N); 1518; 1469; 1235; 760; MS (70 eV/EI): $m/z$ (%) = 313 (M$^+$-HI, 100); $^1$H-NMR (250.1 MHz, DMSO-d$_6$): $\delta$ = 11.15 (s, 1H, C$_6$H$_5$NHNH); 11.01 (s, 1H, C$_6$H$_5$NHNH); 9.35 (s, 1H), 9.19 (s, 1H, NH$_2$); 8.47 (s, 1H, C$_6$H$_5$NHN); 7.73 (m, 2H, H-2'); 7.36 (m, 2H, H-3'); 7.29 (m, 2H, H-3); 7.07 (m, 1H, H-4'); 6.91 (m, 1H, H-4); 6.84 (m, 2H, H-2'); 2.88 (q, 2H, CH$_2$, $J$ = 7.3 Hz); 1.24 (t, 3H, CH$_3$, $J$ = 7.3 Hz); $^{13}$C-NMR (62.9 MHz, DMSO-d$_6$): $\delta$ = 161.1 (N-C-N); 146.8 (C-1); 142.4 (C-1'); 129.3, 129.2 (C-3, C-3'); 123.7 (C-4'); 120.9 (C-4); 117.7 (S=C=N); 116.1 (C-2'); 113.6 (C-2); 27.4 (CH$_2$); 14.8 (CH$_3$).

S-Decyl-thiooxal-1-(2-phenylhydrazono)-2-(2-phenylamidrazonium)bromide (4c)

IR (KBr): $\tilde{\nu}$ (cm$^{-1}$) = 3054, 2955 (NH$_2$); 2924 (NH); 1646, 1601 (C=N); 1497; 1464; 1240; 753; MS (70 eV/EI): $m/z$ (%) = 426 (M$^+$-HBr, 100); $^1$H-NMR (250.1 MHz, DMSO-d$_6$): $\delta$ = 11.10 (s, 1H, C$_6$H$_5$NHNH); 11.01 (s, 1H, C$_6$H$_5$NHNH); 9.36 (s, 1H), 9.20 (s, 1H, NH$_2$); 8.51 (s, 1H, C$_6$H$_5$NHN); 7.72 (m, 2H, H-2'); 7.35 (m, 2H, H-3'); 7.28 (m, 2H, H-3); 7.05 (m, 1H, H-4'); 6.91 (m, 1H, H-4); 6.84 (m, 2H, H-2'); 2.85 (t, 2H, SCH$_2$, $J$ = 7.3 Hz); 1.65-1.15 (m, 16H, H-6-H-13); 0.83 (t, 3H, CH$_3$, $J$ = 7.3 Hz); $^{13}$C-NMR (62.9 MHz, DMSO-d$_6$): $\delta$ = 161.0 (N-C-N); 146.8 (C-1); 142.5 (C-1'); 129.3, 129.2 (C-3, C-3'); 123.6 (C-4'); 120.8 (C-4); 118.1 (S=C=N); 116.0 (C-2'); 113.6 (C-2); 33.0 (SCH$_2$); 31.5 (C-12); 29.6, 29.1 (2x), 28.9 (2x), 28.3 (C-6 - C-11); 22.3 (C-13); 14.2 (CH$_3$).
S-Benzyl-thiooxal-1-(2-phenylhydrazono)-2-(2-phenylamidrazonium)bromide (4d)

IR (KBr): $\tilde{\nu}$ (cm$^{-1}$) = 3380, 3279, 3181 (NH$_2$); 3053 (NH); 1644, 1597 (C=N); 1519; 1497; 1469; 1230; 756; MS (70 eV/EI): m/z (%) = 375 (M$^+$-HBr, 45); 91 (100); $^1$H-NMR (250.1 MHz, DMSO-d$_6$): $\delta$ = 11.19 (s,1H, C$_6$H$_5$NHNH); 10.82 (s,1H, C$_6$H$_5$NHNH); 9.20 (s, 1H), 8.91 (s, 1H, NH$_2$); 8.42 (s, 1H, C$_6$H$_5$NHNH); 7.72 (m, 2H, H-2'); 7.45-7.20 (m, 9H, H-2'', H-3, H-3', H-3'', H-4'''); 7.07 (m, 1H, H-4'); 6.89 (m, 1H, H-4); 6.63 (m, 2H, H-2); 4.15 (s, 2H, CH$_2$); $^{13}$C-NMR (62.9 MHz, DMSO-d$_6$): $\delta$ = 160.9 (N-C-N); 146.7 (C-1); 142.3 (C-1'); 136.7 (C-1''); 129.3, 129.2 (2x), 128.6 (C-2'', C-3, C-3', C-3''); 127.8 (C-4'''); 123.8 (C-4'); 120.7 (C-4); 116.7 (S-C=N); 116.3 (C-2'); 113.6 (C-2); 36.2 (CH$_2$).

S-(4-Nitrobenzyl)thiooxal-1-(2-phenylhydrazono)-2-(2-phenylamidrazonium)bromide (4e)

IR (KBr): $\tilde{\nu}$ (cm$^{-1}$) = 3352 (NH); 3262, 3165 (NH$_2$); 3079 (NH); 1604 (C=N); 1525 (NO$_2$); 1496; 1475; 1346 (NO$_2$); 1256; 753; MS (70 eV/EI): m/z (%) = 420 (M$^+$-HBr, 100); $^1$H-NMR (250.1 MHz, DMSO-d$_6$): $\delta$ = 11.25 (s,1H, C$_6$H$_5$NHNH); 10.82 (s,1H, C$_6$H$_5$NHNH); 9.19 (s, 1H), 8.96 (s, 1H, NH$_2$); 8.40 (s, 1H, C$_6$H$_5$NHNH); 8.17 (m, 2H, H-3'''); 7.71 (m, 2H, H-2''); 7.62 (m, 2H, H-2'''); 7.34 (m, 2H, H-3''); 7.21 (m, 2H, H-3); 7.08 (m, 1H, H-4''); 6.88 (m, 1H, H-4'); 6.62 (m, 2H, H-2); 4.26 (s, 2H, CH$_2$); $^{13}$C-NMR (62.9 MHz, DMSO-d$_6$): $\delta$ = 161.0 (N-C-N); 146.8, 146.7 (C-1, C-1’’); 145.2 (C-4’’); 142.2 (C-1’); 130.8 (C-2’’); 129.1 (2x) (C-3, C-3’); 124.0 (C-4’); 123.7 (C-3’’); 120.8 (C-4); 116.4 (C-2’); 115.8 (S-C=N); 113.5 (C-2); 35.4 (CH$_2$).

X-Ray structure determinations

Crystals of 4b and 4d were sealed onto glass fibres and mounted on a Bruker P4 automated four circle diffractometer (Mo-K$_\alpha$ radiation, $\lambda$ = 0.71073 Å, graphite monochromator). Prior to the automatic cell determination and data collection routines rotational photos were taken to check the
quality of the crystals. The data collection was done in routine $\omega$-scan. Afterwards a Psi-scan was performed in order to do calculations with respect to absorption correction. The structures were solved by direct methods (Bruker SHELXTL) and refined by the full-matrix least-squares method of SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997). Non-hydrogen atoms were refined with anisotropic displacement parameters. Important crystal data as well as bond parameters can be taken from Tables 1-4. Due to the presence of hydrogen donating and accepting groups attempts were made to elucidate the positions of the hydrogen atoms within the NH-groups from the difference maps. Except the hydrogen at N5 in 4b all other positions could be located. These hydrogen position were refined freely while the rest was refined according to the riding model. Crystallographic data (excluding structure factors) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-155603 (4b) and CCDC-155604 (4d). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

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Sample Availability: Samples of compounds 1a-c, 2a, 2b and 4b are available from MDPI.

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