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SYNTHESIS AND PROPERTIES OF SOME DIHYDROTETRAZOLO[5,1-*c*][1,2,4]TRIAZINES.

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Abstract — (5-Mercaptotetrazol-1-yl)acetic acid – nitrile imine acyclic adducts (**12a-c**) undergo intramolecular cyclocondensation, induced by 1,1'-carbonyldiimidazole (CDI), to afford the respective dihydrotetrazolo[5,1-*c*]-[1,2,4]triazines (**13a-c**). The formation of the latter bicycles implies that **12a-c** eject H₂O and undergo S→N migration (Smiles rearrangement) with subsequent expulsion of O=C=S. The structures of **13a-c** were determined by analytical and spectral data, and confirmed by single crystal X-Ray analysis for **13c**.

INTRODUCTION

Synthetic heterocycles incorporating tetrazolo[5,1-*c*][1,2,4]triazine system condensed with naphthalene, e.g. **1**¹, or with benzene e.g. **2**²⁻⁶ were described in the literature (Figure 1). However, there have scarcely been reports on the preparation of the 'parent' bicyclic tetrazolo[5,1-*c*][1,2,4]triazines, such as **3**. A synthetic approach towards **3** utilized suitably functionalized 1,2,4-triazines, being led to the tetrazole ring there-upon. Thus, interaction of nitrous acid with 3-hydrazino-2-methyl-1,2,4-triazine-5-one (**4**) gave a corresponding 3-azido intermediate (**5**) which underwent spontaneous cyclization onto *N*-4 to deliver **3** (Scheme 1).⁷ On the other hand, cyclization of 3-azido-1,2,4-triazine-5-ones (**6**) lacking an alkyl group at *N*-2, occurred preferentially at *N*-2 with ultimate production of the isomeric tetrazolo[1,5-*b*]-[1,2,4]triazine-7-ones (**7A** / Scheme 2).⁷ Likewise, 3-azido-1,2,4-triazine (**8**) cyclized onto *N*-2 to afford tetrazolo[1,5-*b*][1,2,4] triazine (**9A**)⁸ rather than the isomeric tetrazolo[5,1-*c*][1,2,4]triazine (**9B**) (Scheme 2). Such propensity toward cyclization of 3-azido-1,2,4-triazines onto *N*-2 rather than *N*-4 (as exemplified

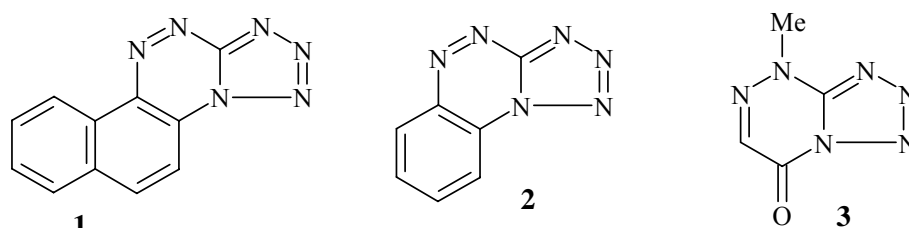
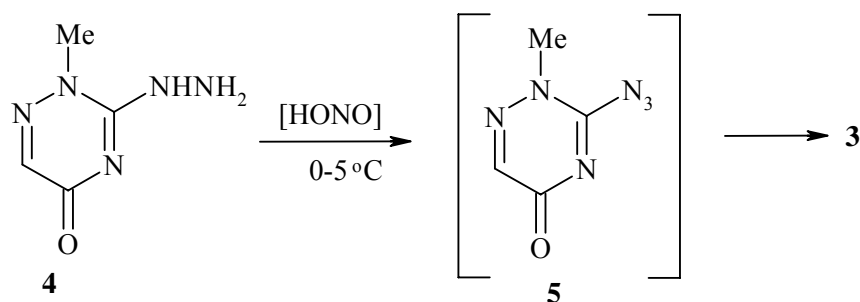
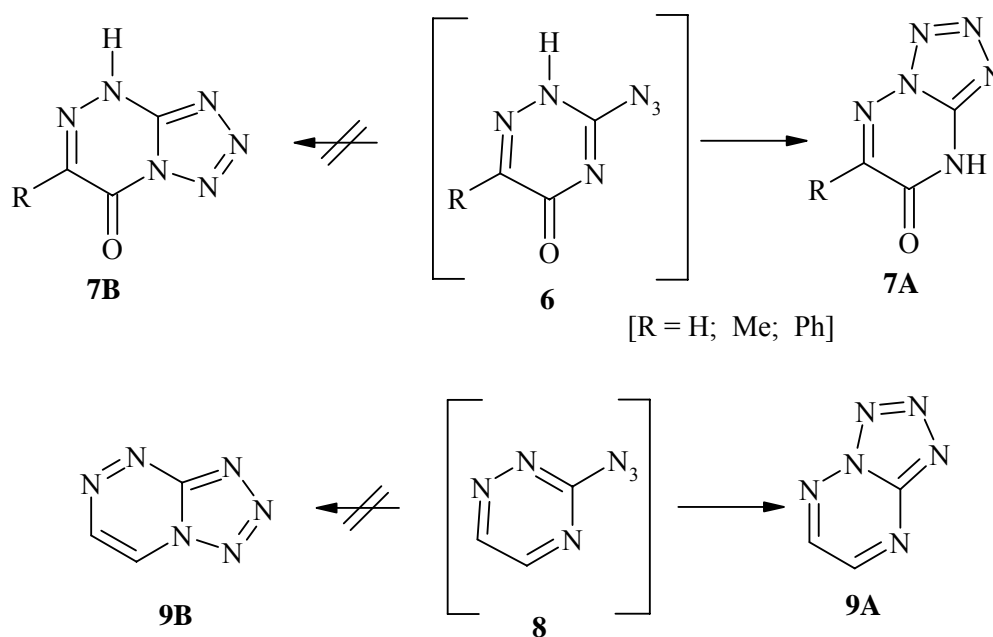


Figure 1



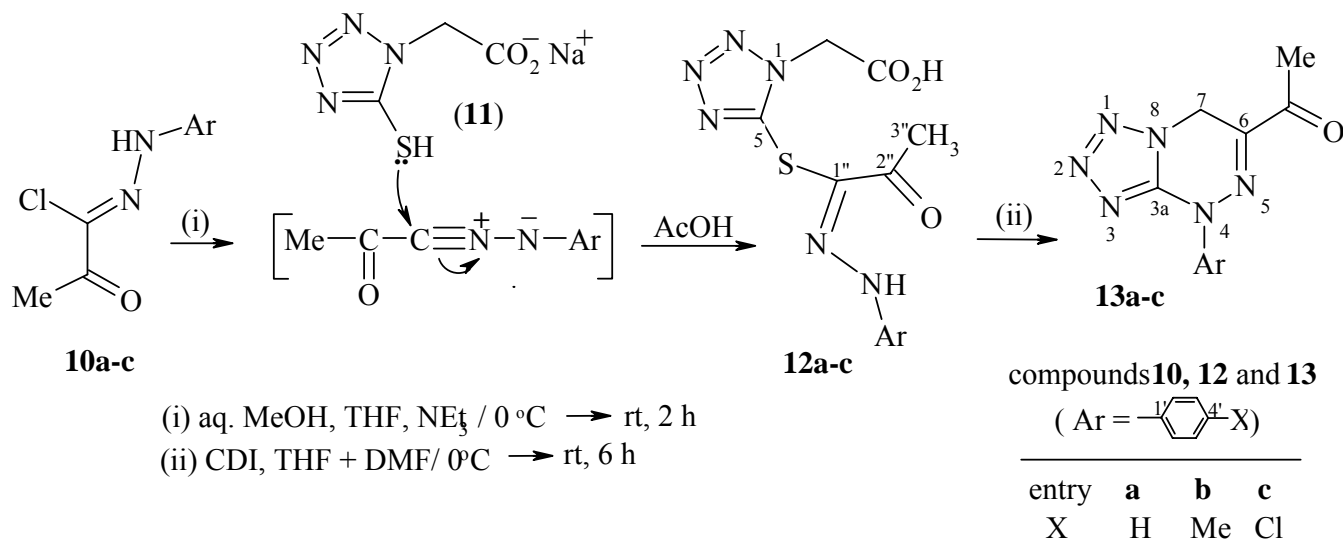
Scheme 1

by **6** and **8** / Scheme 2) poses problematic and limited applicability of this route toward the construction of tetrazolo[1,5-*c*][1,2,4]triazines.



Scheme 2

The present work deals with a new, facile and unique route toward synthesis of model 4,7-dihydro-tetrazolo[5,1-*c*][1,2,4]triazines (**13a-c**), as outlined in Scheme 3.



Scheme 3

RESULTS AND DISCUSSION

Sodium (5-mercaptotetrazol-1-yl)acetate (**11**), acting as sulfur nucleophile in basic medium, adds readily onto the reactive 1,3-dipolar nitrile imines, generated *in situ* from their *N*-arylhyaizonoyl chloride precursors (**10a-c**)^{9,10} by the action of triethylamine, to produce the corresponding 5-[[1-(*N*-arylhyaizonoyl)-2-oxopropyl]thio]-1*H*-tetrazol-1-ylacetic acids (**12a-c**). The latter new adducts (**12a-c**) belong to thiohydrazonates for which a recent review¹¹ has described their preparation, chemistry and utility in organic synthesis. The structure of the acyclic adducts (**12a-c**) is solved on the basis of elemental analyses, MS and NMR spectral data, given in the Experimental part. The ¹H- and ¹³C-NMR of **12** and **13** were assigned from DEPT and 2D (COSY, HMQC and HMBC) data (Scheme 3).¹² In **12a-c**, the ¹³C-nucleus of the carboxyl group resonates at *ca.* 167 ppm, while the Ar-NH proton, showing long range correlations with C-1' and C-1'', appears as a singlet around δ 11.2 ppm. These NH and carboxy signals are, however, not observed in the NMR spectra of the corresponding cyclized products, obtained from the reaction of **12a-c** with 1,1'-carbonyldiimidazole (CDI). The long range correlation is also observed between the methylene protons (H₂-7) and the carbonyl carbon of the C₆-acetyl group in **13a-c**. Besides, these cyclic products lack the sulfur atom, present in **12a-c**, as shown by elemental analyses and MS spectral data. Collectively, these data indicate that H₂O and O=C=S (carbonyl sulfide) are eliminated during the cyclocondensation of **12a-c** as induced by CDI. Eventually the cyclized products were identified as 6-acetyl-4-aryl-4,7-dihydro-1*H*-tetrazolo[5,1-*c*][1,2,4]triazines (**13a-c**), as evidenced from their elemental analyses, IR, MS, ¹H- and ¹³C-NMR spectral data, and confirmed by single crystal X-Ray structure determination for **13c** (Tables 1 and 2, and Figures 2a and 2b).

Table 1. Summary of the crystal data and structure refinement parameters for **13c**.

| | |
|---|--|
| Empirical formula | $C_{11} H_9 Cl N_6 O$ |
| Formula weight | 276.69 Da |
| Temperature | 203(2) K |
| Crystal size | 0.19 x 0.07 x 0.05 mm |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| Unit cell dimensions | $a = 15.2477(18)\text{\AA}$ $b = 7.2736(9)\text{\AA}$ $\beta = 108.203(2)^\circ$ $c = 22.740(3)\text{\AA}$ |
| Volume | $2395.7(5)\text{\AA}^3$ |
| Z | 8 |
| Density (calculated) | 1.534 g cm^{-3} |
| Absorption coefficient | 0.321 mm^{-1} |
| $F(000)$ | 1136 |
| Theta range for data collection | 1.92° to 28.36° |
| Completeness to theta = 28.36° | 99.0 % |
| Index ranges | $-20 \leq h \leq 20$, $-9 \leq k \leq 9$, $-30 \leq l \leq 30$ |
| Reflections collected | 29963 |
| Max. / min. transmission | 1.00 / 0.85 |
| $R_{(\text{merg})}$ before / after correction | 0.0679 / 0.0345 |
| Independent reflections | 5945 [$R_{\text{int}} = 0.0384$] |
| Cell measurement reflections used | 5621 |
| Weighting details | $w = 1 / [\sigma^2 (F_o)^2 + (0.0553 * P)^2 + 3.8116 * P]$ where $P = [(F_o)^2 + 2(F_c)^2] / 3$ |
| Data / restraints / parameters | 4757 / 0 / 349 |
| Goodness-of-fit on F^2 | 1.120 |
| Final R indices [$I > 2 \sigma (I)$] | $R_1 = 0.0581$, $wR_2 = 0.1485$ |
| R indices (all data) | $R_1 = 0.0722$, $wR_2 = 0.1564$ |
| Largest difference peak and hole | 0.679 and $-0.312\text{ e. \AA}^{-3}$ |

Table 2. Selected bond lengths (Å) and angles (°) for the two independent molecule of **13c**, the second molecule has the same numbering scheme but with 20 added.

| | | | |
|------------|--------------------|-----------------|---------------------|
| N(3)–C(3A) | 1.318(3), 1.326(3) | N(3)–C(3A)–N(8) | 110.1(2), 110.5(2) |
| N(3)–N(2) | 1.369(3), 1.371(3) | C(3A)–N(3)–N(2) | 103.9(2), 103.2(2) |
| N(2)–N(1) | 1.290(3), 1.290(4) | N(1)–N(2)–N(3) | 112.1(2), 112.3(2) |
| N(1)–N(8) | 1.351(3), 1.348(3) | N(2)–N(1)–N(8) | 105.8(2), 106.0(2) |
| N(8)–C(3A) | 1.333(3), 1.330(3) | C(3A)–N(8)–N(1) | 108.1(2), 108.0(2) |
| N(8)–C(7) | 1.445(3), 1.448(4) | C(3A)–N(8)–C(7) | 125.1(2), 125.3(2) |
| C(6)–C(7) | 1.510(3), 1.500(4) | N(8)–C(7)–C(6) | 105.92(2), 106.3(2) |
| C(6)–N(5) | 1.284(3), 1.289(3) | N(5)–C(6)–C(7) | 126.4(2), 126.6(2) |
| N(4)–N(5) | 1.373(3), 1.370(3) | C(6)–N(5)–N(4) | 119.0(2), 119.1(2) |
| N(4)–C(3A) | 1.371(3), 1.369(3) | N(8)–C(3A)–N(4) | 119.6(2), 119.9(2) |
| N(4)–C(9) | 1.425(3), 1.426(3) | C(3A)–N(4)–N(5) | 119.4(2), 119.5(2) |
| C(6)–C(15) | 1.495(3), 1.496(4) | C(3A)–N(4)–C(9) | 122.4(2), 122.5(2) |
| O(1)–C(15) | 1.214(3), 1.205(4) | C(15)–C(6)–C(7) | 116.1(2), 116.2(2) |

Both crystallographically independent molecules are linked *via* weak hydrogen bonds, involving the carbonyl groups (O1) and one of the methylene H-atoms (H₂7A) with 2.53 Å (D = 3.259 Å, φ = 98°). Another weak hydrogen bond involving a methyl H-atom (H₃6A) and the carbonyl group at O21 with 2.72 Å (D = 3.664 Å, φ = 166°) is arranged around an inversion center, thus linking four molecules as shown in Figure 2b. The independent molecules have essentially the same geometries and conformation as demonstrated by the torsion angles 32.1 and 30.1° for N25–N24–C29–C34 and N5–N4–C9–C14, respectively.

The formation of **13a-c** implies that the acyclic precursors (**12a-c**) undergo initial loss of H₂O, and *in situ* Smiles rearrangement^{11,13} involving S→N migration; this latter process is experienced by many related thiohydrazonates to afford the corresponding thiohydrazides.^{11,14} A suggested pathway for the transformation of **12a-c** into **13a-c**, is shown in Scheme 4. Thus, intramolecular nucleophilic substitution by the sulfur atom at the activated *N*-carbonyl carbon of [**A**] would produce intermediate [**B**] (Scheme 4). Subsequently, the aryl-NH hooks at the tetrazole carbon-5, displacing the cationic sulfur thereat to afford the respective transient tetrazolo[5,1-*e*][1,3,4,6]thiatriazocin-8(9*H*)-ones [**C**]. Finally, intermediates [**C**] are likely to undergo ring contraction, *via* expulsion of carbonyl sulfide, with ultimate formation of the respective end products (**13a-c**).

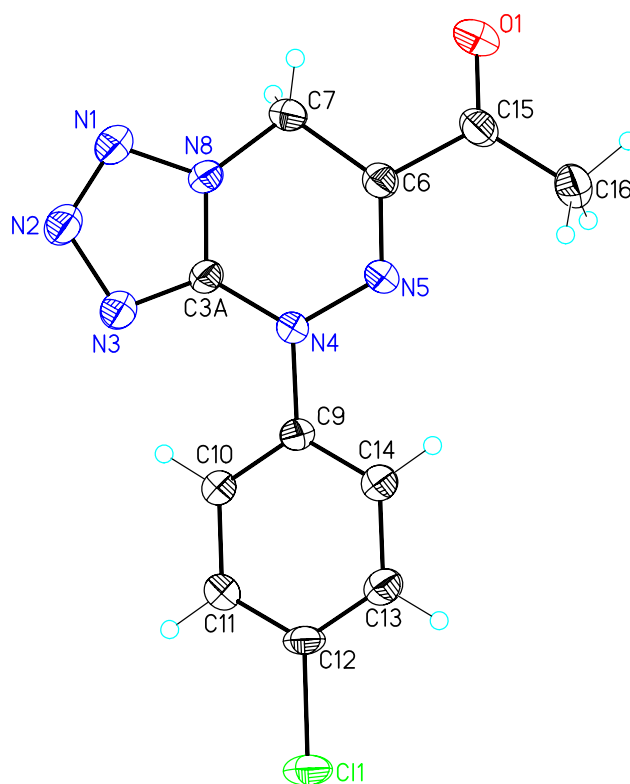


Figure 2a. ORTEP plot (50%) of the molecular structure of **13c**, only one independent molecule with numbering scheme is displayed.

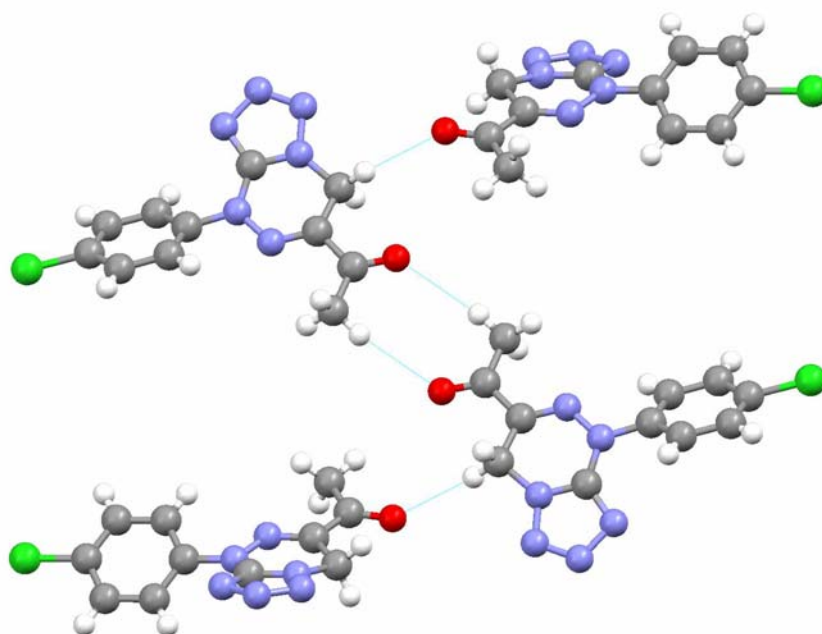
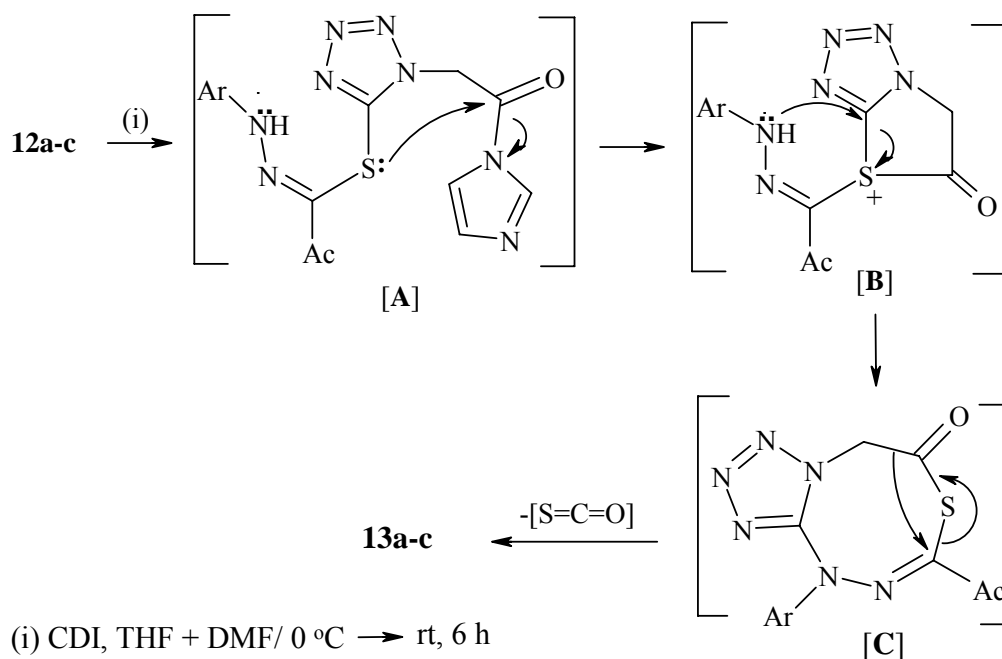


Figure 2b. Arrangement and hydrogen bonds of the two independent molecules in the crystal structure of **13c**, linked *via* the inversion center in Wyckoff letter d.



Scheme 4

In conclusion, CDI effectively transformed those thiohydrazonates (**12a-c**) into the respective tetrazolo[5,1-*c*][1,2,4]triazines (**13a-c**). This unprecedented 'one-pot' reaction utilizes inexpensive synthons, and thus offers a convenient route toward **13a-c** and their analogs. Mechanistically, Smiles rearrangement partakes in the first place, while later steps in this domino reaction are, as yet, not well-understood.

EXPERIMENTAL

5-Mercaptotetrazol-1-ylacetic acid (Na salt), 1,1'-carbonyldiimidazole and 3-chloropentane-2,4-dione were purchased from Acros. Melting points (uncorrected) were determined on a Gallenkamp apparatus. The ^1H - and ^{13}C - NMR spectra were measured on a Bruker DPX-300 instrument with Me_4Si as internal reference. EIMS spectra were obtained using a Finnigan MAT TSQ-70 spectrometer at 70 eV; ion source temperature = 200 °C. High resolution MS-ESI data were obtained with Bruker Bio TOF III. Microanalyses were performed at the Microanalytical Laboratory-Inorganic Chemistry Department, Tuebingen University, Germany.

1-(*N*-Arylhyaazono)-1-chloropropanones (**10a-c**)

These hydrazonoyl chlorides (**10a**),^{9,10} (**10b**)⁹ and (**10c**)^{9,10} were previously characterized, and are prepared in this study *via* the Japp-Klingemann reaction¹⁵ that involves direct coupling of the appropriate aryldiazonium chloride with 3-chloropentane-2,4-dione in aqueous pyridine, following standard procedures.⁹

(5-[[2-Oxo-1-N-(phenylhydrazonyl)propyl]thio]-1H-tetrazol-1-yl)acetic acid (12a)

A solution of sodium 5-mercaptotetrazol-1-ylacetate (**11**) (3.6 g, 20 mmol) in water (25 mL), methanol (5 mL) and triethylamine (10 mL) was added dropwise to a stirred and cooled (0 °C) solution of 1-chloro-1-(phenylhydrazono)propanone (**10a**) (3.9 g, 20 mmol) in tetrahydrofuran (50 mL). Upon completion of this addition, the reaction mixture was allowed to stir at 0-5 °C for additional 2 h. The organic solvents were then removed from the reaction mixture *in vacuo*, the remaining aqueous solution was acidified with acetic acid, and extracted with dichloromethane (2 x 40 mL). The combined organic extracts were in turn washed with water (40 mL), and then dried (MgSO₄). The solvent was evaporated at reduced pressure to give a solid product which was purified by column chromatography (SiO₂, eluting with CH₂Cl₂ - MeOH, 20 : 1 v/v). Yield = 2.9 g (45 %); mp 215-216 °C. *Anal.* Calcd for C₁₂H₁₂N₆O₃S: C, 45.00; H, 3.78; N, 26.24; S, 10.01. Found: C, 44.82; H, 3.72; N, 26.08; S, 9.88; EI MS *m/z* (%): 320 (6, M⁺), 277 (17), 232 (72), 217 (6), 194 (14), 176 (8), 160 (24), 135 (37), 131 (27), 118 (100), 92 (28), 91 (90), 77 (48), 43 (59), HRMS: calcd. for C₁₂H₁₂N₆O₃S: 320.06912, found 320.07093; ¹H NMR (300 MHz, DMSO-*d*₆): δ 2.44 (s, 3H, COCH₃), 5.21 (s, 2H, CH₂COOH), 7.03 (tt, *J* = 7.4, 1.1 Hz, 1H, H-4'), 7.31 (dd, *J* = 8.4, 7.4 Hz, 2H, H-3'/H-5'), 7.42 (dd, *J* = 8.4, 1.1 Hz, 2H, H-2'/H-6'), 11.15 (s, 1H, C(1')-NH); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 25.8 (COCH₃), 50.2 (CH₂COOH), 115.8 (C-2'/C-6'), 124.0 (C-4'), 124.7 (C-1''), 129.8 (C-3'/C-5'), 142.9 (C-1'), 151.0 (C-5), 167.5 (CO₂H), 192.2 (Me-C=O).

(5-[[1-N-(4-Methylphenylhydrazonoyl)-2-oxopropyl]thio]-1H-tetrazol-1-yl)acetic acid (12b)

This compound was prepared by the reaction of **11** with 1-chloro-1-[(4-methylphenyl)hydrazono]propanone (**10b**) (4.2 g, 20 mmol) as described above for **12a**. Acidification of the reaction mixture gave a solid product which was washed with cold methanol (6 mL), and then diethyl ether (3 x 10 mL). The product was further purified using column chromatography (SiO₂, eluting with CH₂Cl₂ - MeOH, 20 : 1 v/v), and recrystallized from ethanol. Yield = 3.8 g (57 %); mp 223-224 °C. *Anal.* Calcd for C₁₃H₁₄N₆O₃S: C, 46.70; H, 4.22; N, 25.14; S, 9.59. Found: C, 46.83; H, 4.11; N, 24.86; S, 9.45; EI MS *m/z* (%): 334 (6, M⁺), 291 (14), 246 (46), 208 (16), 174 (12), 160 (15), 149 (18), 132 (100), 105 (85), 91 (43), 77 (18), 43 (35), HRMS: calcd. for C₁₃H₁₄N₆O₃S: 334.08477, found 334.08621; MS (TOF ES⁺): *m/z* 357 (M+Na)⁺, HRMS: calcd. for C₁₃H₁₄N₆O₃S 1Na: 357.0746, found 357.0740; ¹H NMR (300 MHz, DMSO-*d*₆): δ 2.21 (s, 3H, C(4')-CH₃), 2.44 (s, 3H, COCH₃), 5.06 (s, 2H, CH₂COOH), 7.09 (d, *J* = 8.1 Hz, 2H, H-3' / H-5'), 7.31 (d, *J* = 8.1 Hz, 2H, H-2' / H-6'), 11.24 (s, 1H, C(1')-NH); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 20.9 (C(4')-CH₃), 25.8 (COCH₃), 50.9 (CH₂COOH), 115.8 (C-2'/C-6'), 123.8 (C-1''), 130.1 (C-3'/C-5'), 133.0 (C-4'), 140.8 (C-1'), 150.6 (C-5), 167.1 (CO₂H), 192.2 (Me-C=O).

(5-[[1-N-(4-Chlorophenylhydrazonoyl)-2-oxopropyl]thio]-1H-tetrazol-1-yl)acetic acid (12c)

This compound was prepared by reacting **11** (3.6 g, 20 mmol) and 1-chloro-1-[4-

chlorophenyl)hydrazono]propanone (**10c**) (4.6 g, 20 mmol) as described for **12a**, and the reaction mixture was worked-up as described for **12b** above. Yield = 3.7g (52 %); mp 235-236 °C. *Anal.* Calcd for C₁₂H₁₁N₆O₃ClS: C, 40.63; H, 3.13; N, 23.69; S, 9.04. Found: C, 40.35; H, 3.02; N, 23.61; S, 8.79; EI MS *m/z* (%): 354 (2, M⁺), 311 (21), 281 (11), 266 (74), 253 (7), 228 (14), 221 (6), 196 (10), 169 (45), 152 (96), 125 (100), 111 (45); HRMS: calcd. for C₁₀H₈N₆O₂ClS (M-Ac) 311.01176, found 311.01440; ¹H NMR(300 MHz, DMSO-*d*₆): δ 2.45 (s, 3H, COCH₃), 5.24 (s, 2H, CH₂COOH), 7.36 (d, *J* = 8.4Hz, 2H, H-3'/H-5'), 7.44 (d, *J* = 8.4 Hz, 2H, H-2'/H-6'), 11.24 (s, 1H, C(1') -NH); ¹³C NMR(75 MHz, DMSO-*d*₆): δ 25.9 (COCH₃), 50.5 (CH₂COOH), 117.3 (C-2'/C-6'), 125.8 (C-1'), 127.6 (C-4'), 129.7 (C-3'/C-5'), 141.9 (C-1'), 150.8 (C-5), 167.9 (CO₂H), 192.2(Me-C=O).

6-Acetyl-4-phenyl-4,7-dihydro-tetrazolo[5,1-*c*][1,2,4]triazine (13a)

1,1'-Carbonyldiimidazole (0.5 g, 3.0 mmol) was added to a stirred and cooled (0 °C) solution of **12a** (0.8 g, 2.5 mmol) in dry tetrahydrofuran (60 mL) and dry DMF (2 mL). The reaction mixture was stirred at 0-5 °C for 2 h, and then at rt for 4 h. During this time, the initial pale yellow solution acquired bright yellow color that changed gradually to orange, and finally reddish-coloration. Water (50 mL) was added to the reaction mixture which was then concentrated *in vacuo* to about 40 mL and extracted with dichloromethane (2 x 40 mL). The combined organic extracts were washed with water (30 mL), dried (MgSO₄) and the solvent was evaporated. The residual solid product was purified by column chromatography (SiO₂, eluting with CH₂Cl₂ - MeOH, 20 : 1 v/v) and recrystallized from ethanol. Yield = 0.28 g (43 %); mp 188-189 °C. *Anal.* Calcd for C₁₁H₁₀N₆O: C, 54.54; H, 4.16; N, 34.69. Found: C, 54.42; H, 4.12; N, 34.36; MS (TOF ES⁺): *m/z* 243 (M+H)⁺, HRMS: calcd. for C₁₁H₁₀N₆O 1H: 243.0994, found 243.0989; ¹H NMR(300 MHz, DMSO-*d*₆): δ 2.47 (s, 3H, COCH₃), 5.27 (s, 2H, H₂-7), 7.32 (t, *J* = 7.4 Hz, 1H, H-4'), 7.53 (dd, *J* = 8.0, 7.4 Hz, 2H, H-3'/H-5'), 7.88 (d, *J* = 8.0 Hz, 2H, H-2'/H-6'); ¹³C NMR(75 MHz, DMSO-*d*₆): δ 25.1 (COCH₃), 44.0 (C-7), 120.7 (C-2'/C-6'), 126.8 (C-4'), 129.7 (C-3'/C-5'), 139.7 (C-6), 140.7 (C-1'), 147.1 (C-3a), 195.1(Me-C=O).

6-Acetyl-4-(4-methylphenyl)-4,7-dihydro-tetrazolo[5,1-*c*][1,2,4]triazine (13b)

This compound was prepared from CDI (0.5 g, 3.0 mmol) and **12b** (0.84 g, 2.5 mmol) by following the procedure and experimental conditions described above for obtaining **13a**. Yield = 0.32 g (47 %); mp 140-141 °C. *Anal.* Calcd for C₁₂H₁₂N₆O: C, 56.24; H, 4.72; N, 32.79. Found: C, 56.02; H, 4.58; N, 32.61; MS (TOF ES⁺): *m/z* 257 (M+H)⁺, HRMS: calcd. for C₁₂H₁₂N₆O 1H: 257.1151, found 257.1152; *m/z* 279 (M+Na)⁺, HRMS: calcd. for C₁₂H₁₂N₆O 1Na: 279.0970, found 279.0965; ¹H NMR(300 MHz, DMSO-*d*₆): δ 2.32 (s, 3H, C(4') CH₃), 2.45 (s, 3H, COCH₃), 5.25 (s, 2H, H₂-7), 7.32 (d, *J* = 8.1 Hz, 2H, H-3'/H-5'), 7.73 (d, *J* = 8.1 Hz, 2H, H-2'/H-6'); ¹³C NMR(75 MHz, DMSO-*d*₆): δ 21.0 (C(4') -CH₃), 25.1 (COCH₃), 44.0 (C-7), 120.9 (C-2'/C-6'), 130.1 (C-3'/C-5'), 136.3 (C-4'), 138.4 (C-1'), 139.4 (C-6), 147.2 (C-3a),

195.1(Me-C=O).

6-Acetyl-4-(4-chlorophenyl)-4,7-dihydro-1H-tetrazolo[5,1-c][1,2,4]triazine (13c)

This compound was prepared from CDI (0.5 g, 3.0 mmol) and **12c** (0.74 g, 2.5 mmol) by following the procedure and experimental conditions noted above for obtaining **13a**. Yield = 0.39 g (53 %); mp 183-184 °C. *Anal.* Calcd for C₁₁H₉N₆OCl: C, 47.75; H, 3.28; Cl, 12.81; N, 30.37. Found: C, 47.52; H, 3.26; Cl, 12.74, N, 30.12; MS (TOF ES⁺): *m/z* 277 (M+H)⁺, HRMS: calcd. for C₁₁H₉N₆OCl 1H: 277.0605, found 277.0599; ¹H NMR(300 MHz, DMSO-*d*₆): δ 2.46 (s, 3H, COCH₃), 5.26 (s, 2H, H₂-7), 7.59 (d, *J* = 8.5 Hz, 2H, H-3'/H-5'), 7.94 (d, *J* = 8.5 Hz, 2H, H-2'/H-6'), ¹³C NMR (75 MHz, DMSO-*d*₆): δ 25.2 (COCH₃), 44.1 (C-7), 122.1 (C-2'/C-6'), 129.7 (C-3'/C-5'), 130.7 (C-1'), 139.5 (C-4'), 140.1 (C-6), 147.0 (C-3a), 195.1(Me-C=O).

COLLECTION OF X-RAY DIFFRACTION DATA AND STRUCTURE ANALYSIS OF 13c

Colorless needles were grown by allowing a clear solution of **13c** in hot ethanol to stand at room temperature for 4 – 5 days. Crystal data collection was made with a Siemens SMART CCD diffractometer [Mo-K α -radiation, graphite monochromator] operating in the omega scan mode (0.3°). The data were reduced with the Siemens-Bruker program suite XSCANS¹⁶ and the structure was solved by the direct method using SHELXTL PLUS programs.¹⁷ All non-hydrogen atoms were refined anisotropically by full-matrix, least-squares procedure based on *F*² using all unique data. Hydrogen atoms were placed in calculated positions and treated as riding groups, with the 1.2 fold (1.5 fold for methyl groups) isotropic displacement parameters of the equivalent U_{ij} of the corresponding carbon atom.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis of **13c** have been deposited with the Cambridge Crystallographic Data Center under the depository No. CCDC-299044. Copies of information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: (deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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